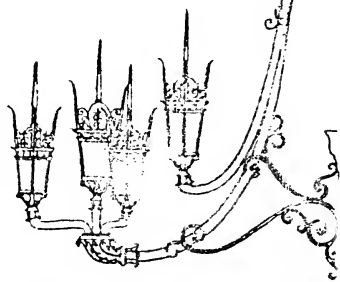


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INVESTIGATIONS ON THE THEORY  
OF THE  
PHOTOGRAPHIC PROCESS



INVESTIGATIONS ON THE THEORY  
OF THE  
PHOTOGRAPHIC PROCESS

BY

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“ Neither more nor more onerous causes are to be assumed, than are necessary  
to account for the phenomena.”—WILLIAM OF OCCAM.

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TO  
SIR WILLIAM RAMSAY, K.C.B., F.R.S.  
WHOSE CONTINUED INTEREST AND ADVICE  
HAS INSPIRED THIS WORK





## P R E F A C E

It must be understood that the following pages are in no sense a text-book or an authoritative pronouncement on the theory of negative making, but simply a collection of certain investigations carried out in the past four years. A preface is frequently an apology for what follows, and to some extent this is the case with our own. For the possibly objectionable wealth of experimental details and results, it must be pleaded that the work was first presented in theses for degrees, and could not be subsequently cut down without a most radical alteration. Also, comprehensive and minute details, though frequently taking too much space for their publication in the ordinary journals, are sometimes of value to other investigators, who may draw from them other, and more correct, conclusions than their originators.

We hope, however, that the work is sufficiently comprehensive to be of value to those photographers interested in the bases of their hobby or profession, to the experimental investigator in photography, and to the scientific student of photographic chemistry. In our investigations we have always endeavoured to deal with questions quantitatively, feeling that only in this way can any advance of permanent value be made.

Much of the work has been previously published as separate papers, and we have to express our thanks to the following

Societies for permission to reproduce the matter, which in some cases has been amplified or altered, viz. to the Royal Society, the Chemical Society, and the Royal Photographic Society.

In accordance with the regulations of the University of London, these researches have been accepted as theses, the earlier portions for the degree of Bachelor of Science by research, the later for the degree of Doctor of Science.

S. E. SHEPPARD.

C. E. K. MEES.

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# INVESTIGATIONS ON THE THEORY OF THE PHOTOGRAPHIC PROCESS

## PART I. *INTRODUCTORY*

### CHAPTER I

#### THE BEARING OF PHYSICAL CHEMISTRY ON DEVELOPMENT

THE few pages here are intended as a brief introduction to photographers into the grammar of physical chemistry. They formed part of a lecture delivered before the Royal Photographic Society, as an introduction to some of the subsequent matter of this book. They are, of course, a very inadequate presentation of the theory of solutions and its cognate subjects. Those photographers desiring to study this development of chemistry further may refer to *An Introduction to Physical Chemistry*, by J. Walker (Macmillan), and for a more detailed and advanced treatment, to the series of text-books edited by Sir William Ramsay, and published by Longmans, in especial to *Chemical Statics and Dynamics*, by J. W. Mellor. The essential of physical chemistry lies not in its matter but its method, in the application of physical and quantitative methods to chemical problems.

Historically it is still young—may, in fact, be said to have just come of age—yet it is already reacting powerfully on the theories and methods of its parent sciences. To define exactly its scope would be difficult, and it is the less necessary in that we are here chiefly concerned with two of its branches,

the theory of solutions, and chemical dynamics, or, as we might term them, the condition and the course of chemical change.

Let us see, to start with, what is now understood by a solution. You are all practically familiar with aqueous solutions of such bodies as sugar, salt, or "pyro." And you know that however much you mechanically subdivide this solution, each portion still exhibits the same specific properties as the whole. Now this introduces us to a very important conception, namely, that of a "phase." *In any system, every part of it which shows identical properties we term a phase.* The degree of division is immaterial; thus a million particles of chalk suspended in water form a single phase; so do the numerous grains of silver haloid in an emulsion. But suppose we introduce energy into the system from without—by heat, for example. Beyond a certain limit of temperature and pressure a new phase is formed from the first, thus our aqueous solution evaporates. Moreover, the residue of the solution becomes denser as the process proceeds, the vapour less dense. Such is not the case on evaporating pure water. Both residue and vapour keep the same properties, and such a body is termed "hylotropic." This is nearly the same conception as that of a chemical individual, and for present purposes we may take it as such. Solutions can always be separated into a finite number of hylotropic bodies, from which the same solution can again be compounded. And a chemical compound is only a special case of a solution in which the proportion of the components remains constant within certain limits of temperature and pressure. (Those who wish to follow the application of this to the fundamentals of chemistry, the doctrine of constant, etc., proportions, should read Ostwald's "Faraday" Lecture, *Journ. Chem. Soc.*, 1904, 85. 506.)

The extremely general nature of solution is now obvious, and we must remember that solutions may occur in any of the so-called "states of matter," solid, liquid, or gaseous.

Leaving this line of argument, let us return to our aqueous solution. It is common to distinguish between "solvent" and "solute," the body dissolved. The foregoing discussion shows

that the distinction is arbitrary. Solution is a general condition, of which chemical combination is a special case. But in the region of dilute solution, the conditions of which are best known to us, the distinction is useful, and a valuable conception has been evolved from it. A solution is dilute when one component is present in relatively small proportion. And the conception at the back of most modern work is that *the "solvent" affords a free space for action for the "solute," but is otherwise inert.* In other words, it acts as a vacuum, in which the solute behaves as a gas. It is probable that this concept has nearly reached the maximum of its utility, and that as investigation is turned more to concentrated solutions, modifications of this view will become necessary.

Meanwhile, however, let us accept what has been obtained. Just as a gas confined to a definite volume exerts a pressure, so does a dissolved body. This pressure is termed "osmotic" pressure, and its existence is evident from the diffusion of bodies in solution. We know that if we put a strong solution at the bottom of a vessel and add without mixing more water, in course of time the solution will become equal in strength throughout. Osmotic pressure may be measured directly by the hydrostatic pressure generated in vessels with semi-permeable membranes, or indirectly by the lowering of the freezing point of the solution or the raising of its boiling point. And it is found that the same laws hold as for gaseous pressure. Firstly, Boyle's law, that at constant temperature the pressure is inversely proportional to the volume, *i.e.* directly proportional to the concentration. Secondly, Gay-Lussac's law, that at constant volume the pressure is directly proportional to the absolute temperature. Finally, if we dissolve bodies in proportion to their molecular weights we obtain the same osmotic pressure, whence we infer that Avogadro's hypothesis applies to solution. This states that equal volumes of gases at the same temperature and pressure contain equal numbers of molecules, so that the analogy between gas and osmotic pressure is complete.

It was soon found, however, that for a large class of substances the osmotic pressure was in excess of that calculated

from the molecular weight. A similar result is frequently obtained for vapour-pressure. Thus  $\text{N}_2\text{O}_4$  gives pressures in excess of that calculated from its formula. In all such cases this is found to be due to the *dissociation* or splitting up of the body; in our example  $\text{N}_2\text{O}_4 \rightarrow 2\text{NO}_2$ . Furthermore, it was found that the bodies which in solution gave this excess pressure were those which form solutions conducting electricity or electrolytes. Now Kohlrausch had shown that the conductivity of electrolytes is additively composed, at great dilution, of that of two components, the positive and negative ion postulated by Faraday as the carriers of the current in electrolysis. Arrhenius, then, from somewhat scanty data, put forward the hypothesis of electrolytic dissociation. Electrolytes in solution are conceived as splitting into a positive and negative ion, each associated with one or more charges of electricity. Taking a simple case—



sodium as positive ion or kation, chlorine as negative or anion. We must remember that we have not here sodium and chlorine in solution, but new substances, sodion and chlorion, with distinct properties.

It would take far too long to enter into all the evidence for and against this theory. But at least we may say that the evidence in favour is much superior in bulk and quality, by which we understand agreement between calculation and observation, to that against it. And it has yet to be shown that the theory is not sufficiently flexible to embrace the apparent exceptions.

Meanwhile let us examine a few applications. We speak of acids, bases, and salts as classes of bodies exhibiting similar properties in solution. The ionic theory gives a simple explanation of this. Acids are bodies which in solution form hydrogen ions. Thus  $\text{XH} \rightarrow \text{X}' + \text{H}^+$ , and their common properties, are those of hydrion  $\text{H}^+$ . Similarly bases or alkalis give hydroxyl ions,  $\text{YOH} \rightarrow \text{Y}' + \text{OH}'$ . The "strength" of an acid or alkaline solution depends upon the amount it contains of hydrion or hydroxylon. Salts are produced by



the interaction of an acid and a base, and have a positive ion, generally a metal, and a negative ion. All salts with the same kation exhibit the properties of this, which explains the validity of the usual analytical tests for all salts of the same metal. In terms of this theory, most of our ordinary analytical reactions are "ionic," and the same may be said of photographic reactions. Hence to obtain clearer views about these it is desirable to know what the reacting ions are.

Before applying the theory in any detail to development, we will consider the other branch of physical chemistry mentioned, chemical dynamics or the theory of chemical change. Generally speaking, change means a state varying with time, and from this we obtain the conception of equilibrium, as *a state independent of time*. The idea of equilibrium in mechanics was derived from the balancing of weights, but what do we mean by chemical equilibrium? Suppose a body AB in solution splits up into A and B. We indicate such a reaction by  $AB \rightleftharpoons A + B$ , and usually understand the reaction to proceed entirely in the direction of the arrow. But very many chemical reactions are reversible, *i.e.* proceed in either direction according to the conditions. To denote this we write our reaction  $AB \rightleftharpoons A + B$ . We now wish to know, how does the rate of change and the final equilibrium depend upon the quantities present of the bodies? This brings us to two conceptions, that of the velocity of reaction, and of the "active mass" of a body. You know that in mechanics velocity is measured by the distance covered divided by the time, which we write  $s/t$ , feet per second, for example. Just so chemical velocity is measured by the quantity of substance changed divided by the time,  $x/t$ , or, if we consider not average but actual velocity,  $dx/dt$ . This we will call  $v$ . Now, Guldberg and Waage put forward the view that velocity  $v$  was proportional to the "active mass" of the body undergoing change. We may consider this "active mass" to be in most cases the molecular concentration of the body, *i.e.* the number of gramme-molecules divided by the volume. For our chemical change  $AB \rightleftharpoons A + B$  we have  $v_1$ , the velocity, proportional to the concentration, or  $v_1 = K_1 C_{AB}$ , while for the velocity of the reverse action  $A + B \rightleftharpoons AB$  we

get  $v_2 = K_2 C_A \times C_B$ . Then the actual velocity at any time is  $v = (v_1 - v_2) = K_1 C_{AB} - K_2 C_A \times C_B$ . At equilibrium by definition  $v = 0$ , hence  $v_1 = v_2$ , or  $K_1 C_{AB} = K_2 \cdot C_A \cdot C_B$ . *Chemical equilibrium is reached when the velocities of two opposing processes are equal* and is dynamic in its nature. The foregoing example is a special case of the law of mass-action, one of the most fruitful inductions in physical chemistry. We will now examine the case where one reacting body is a solid. How shall we represent the active mass of a solid? Returning a moment to our initial discussion of "solution" and "phase," this means that our system contains more than one "phase," and is therefore termed "heterogeneous."

The answer to our question can be deduced from the statement, *chemical action can only take place in one phase, necessarily a solution*. Thus modern chemistry has revived an old adage of mediæval alchemy, "*corpora non agunt nisi soluta*." There is no such thing, for instance, as a chemical reaction between a solid and a liquid. When chalk is "dissolved" by an acid, there is always a small quantity of chalk dissolved in the water, and this constitutes its "active mass," which reacts with the acid. At equilibrium, the active mass of the chalk or other solid is constant, *for the solution is saturated with respect to it*, and is independent of the amount present as solid. Thus suppose in our former reaction AB were present as solid. We had  $K_1 C_{AB} = K_2 C_A \times C_B$ , but since  $C_{AB}$  is now constant, we find that the product of  $C_A$  and  $C_B$  is constant, a case experimentally realisable by heating solid ammonium hydrosulphide—



If we measure the partial pressures of the ammonia and sulphuretted hydrogen at equilibrium, we shall find their product is constant and independent of the amount of solid hydrosulphide. We may generalise our results as follows:—Every substance is more or less soluble, or has a definite "solution pressure," and its activity in solution is measured by its concentration. If we apply this to development, it follows that the chemical reaction in the process is between the small

portion of silver bromide dissolved in water and the developer. Further, the silver bromide will be "ionised," and as its solubility is so slight, nearly completely according to the equation  $\text{AgBr} \rightleftharpoons \text{Ag}^+ + \text{Br}^-$ . The reaction is really between the silver kation and the reducing ion, and simply consists in the transference of electrical charges according to the equation—



Moreover, the equation  $\text{AgBr} \rightleftharpoons \text{Ag}^+ + \text{Br}^-$  explains the action of soluble bromides in restraining development. Increasing the active mass of the bromide ion must lower that of the silver ion, since that of the undissociated silver bromide is constant. As a matter of fact, the influence of bromide is chiefly limited to the initial stage of development, the complete explanation of which we must postpone. We may say, however, that in general ionic reactions are, as we should expect, immeasurably rapid, and our investigations indicate that the velocity of development does not depend normally upon that of the chemical processes. But this brings us to the experimental measurement of the velocity of development. This is done by measuring the mass of silver reduced and plotting it against the time. The mass of silver is obtained photometrically, being proportional to Hurter and Driffeld's "density." It is found that the density on greatly prolonging development reaches a limit depending only on the exposure. It seems reasonable to suppose that this  $D_x$  represents for each exposure the total amount of silver bromide rendered developable by light. And further it is evident that the velocity of development  $dD/dt$  depends upon this  $D_x$ . Now previously we have stated that velocity depends upon the "active mass," and that this in the case of a solid body is independent of the amount of solid. How, then, does  $D_x$ , the amount of solid AgBr developable, influence the velocity? The fact is that the mass-action law is only true for the one phase, and that when we have chemical action in so-called heterogeneous systems the actual reaction takes place in a thin layer bounding the phases. The velocity then often depends not upon that of the chemical reaction, but on the rate with

which the reacting bodies get into this layer. An example may make clear the bearing of this. If you send a telegram, it is not the actual transmission by wire which occupies time—that operation is practically instantaneous—but its delivery by the more or less laggard telegraph boy. Reactions which take place in stages are known as “graded” reactions, and while their course may be simple if one stage is slow compared with the others, if this is not so complications in the mathematical description are necessary. In development we have a number of particles surrounded by developer, and the reaction takes place in a very thin layer surrounding these. If we consider the chemical reaction to be relatively fast, then the velocity will depend upon the number or rather surface of these particles, and on the diffusion to this surface of the reducing ion. Now this surface is originally  $D_x$ , but when an amount of silver,  $D$ , has been reduced, it becomes  $D_x - D$ . Further, if the concentration outside the layer be  $a$  and the thickness of its diffusion path be  $\delta$ , the general law for diffusion shows that the velocity will be  $S \cdot \Delta \cdot a/\delta$ , where  $S$  is the surface, and  $\Delta$  is a specific constant of the reducing ion, termed its diffusivity. We get for the

velocity at any time therefore  $\frac{dD}{dt} = \frac{\Delta a}{\delta} (D_x - D)$ , or writing  $K$  for  $\Delta a/\delta$ , and summing up by the process of integration all the values of  $\frac{dD}{dt}$ , we obtain  $K = \frac{1}{t} \log \frac{D_x}{D_x - D}$ ; this  $K$  we term the velocity constant of development, since it remains unchanged over a large range of development when both  $t$  and  $D$  vary. Its meaning is simply this: it is the fraction of the original density which would be developed in unit time if all the conditions kept in the same state.

Since  $\gamma$ , Hurter and Driffeld's development factor, is proportional to the density  $D$ , we have the same law for the growth of this, or—

$$K = \frac{1}{t} \log \frac{\gamma_x}{\gamma_x - \gamma}$$

and we can for the same emulsion use this constant to measure the relative velocities of varying developers under different

conditions. Thus  $K$  is proportional to the concentration of the reducing ion. This we should expect, for in diffusion the rate at which an ion travels is proportional to the osmotic pressure urging it on, and therefore to the concentration. Similarly  $K$  increases with the temperature, and generally is affected by all conditions altering the diffusivity. A very marked alteration is produced, for example, when plates are stored under unfavourable conditions of temperature and atmosphere.

## CHAPTER II

### INSTRUMENTS AND METHODS OF WORKING

**General.**—Since the year 1880 a large number of instruments have been designed with a view to the expression of the diverse phenomena exhibited by photographic plates in the form of numerical constants attainable by simple experiment.

The most notable step in this direction was that made by Messrs. Hurter and Driffeld when they devised their system of speed determination. Their system of speed determination, however, does not include any expression of the developing properties of a plate. In the *Photographic Journal*, February and July, 1903, we showed that the developing properties of a plate can be completely expressed in numerical constants, and explained a method by which those constants could be determined.

In the course of a general investigation of photographic plates we have modified and designed a series of instruments by means of which the whole of the properties of a plate can be rapidly and simply determined as a series of sensitometric constants.

These instruments include (1) an instrument for impressing a graduated series of accurately known exposures upon the plate ; (2) an instrument for developing the plate for a known time at a known temperature ; (3) an instrument for accurately measuring the densities obtained.

#### SENSITOMETERS.

Sensitometers are composed of two integral portions, which will be discussed separately.

(a) Constant light source.

(b) The exposing apparatus, *i.e.* a device for impressing an increasing series of exposures upon a plate.

(a) *Constant Light Sources.*

The question of light sources and standards is co-eval with photometry, and can only be briefly discussed here. We may distinguish between primary and secondary standards, of which the second are the most important for sensitometry.

**Primary Standards.**—For a description of various primary standards proposed and adopted, the reader is referred to any standard work on photometry and to the bibliography appended. A primary standard has not only to fulfil the condition of keeping accurately constant, but also of being easily reproducible, as it is intended to serve as the unit of light intensity. The chief primary standards which have been proposed are the standard candle (in England as defined by Act of Parliament), the Vernon-Harcourt pentane lamp, and the smaller Simmance modification of the same. As we have used the latter form as a reference standard for calibrating our own constant light sources, some description may be of interest. Air passes over about 4 lineal feet of pentane surface. The descent by gravity of the resultant gas automatically governs the air supply. The pentane, the length of fall, the height of the flame, and its intensity are always the same. It is equal to one standard spermaceti candle burning 120 grains per hour, and by comparison equal to one-tenth Harcourt standard, adopted as the standard light unit in London. Another popular standard is the Hefner-Altneck lamp, in which pure amyl acetate is burnt.<sup>1</sup>

Other standards proposed are the Carcel lamp, and the Platinum Standard, this being the intensity of light given by a definite weight of platinum kept at a definite temperature (*e.g.* the melting-point).

The Netherlands Commission, 1894,<sup>2</sup> decided that the

<sup>1</sup> *Eder's Jahrbuch f. Phot.*, 1892, 98.

<sup>2</sup> Ref. by H. Krüss, *Journ. f. Gasbeleuchtung*, 1894.

platinum standard was impracticable, that the Hefner lamp was good, but the Harcourt pentane standard was better.<sup>1</sup> Either seems preferable to the standard candle.

**Secondary Standards.**—As constant light sources pure and simple, many arrangements have been adopted. Hurter and Driffield in their well-known researches used the standard candle,<sup>2</sup> Sir W. de W. Abney has used the amyl acetate lamp, and Dr. J. M. Eder, in his important work on Sensitometry, the Benzin-Kerze.<sup>3</sup> The pentane light has also been used, and Dr. Vogel has recommended the use of magnesium ribbon, both the length and weight being kept constant.<sup>4</sup>

As an electrical standard a glow-lamp run off accumulators and controlled by a potentiometer may be used, but it must be noticed that the intensity is proportional to a very high power of the voltage.

We have in our own researches used pure acetylene gas burning under constant pressure; for accurate work the flame being screened and only a small area used.

J. Violle<sup>5</sup> proposed an acetylene standard in 1895, the acetylene streaming out of a small conical opening into a broader tube, where it mixes with air, and is then burnt in a flat "butterfly" burner. This mixing is accomplished satisfactorily in the modern acetylene burners of the Naphey type.<sup>6</sup>

In our investigations we used originally a special form of gas-holder with a very small water surface,<sup>7</sup> the gas being passed into this from a Tylar "Dreadnought" generator. The gas passed then through a two-way stop-cock, one leading

<sup>1</sup> But see the researches of Liebenthal mentioned later.

<sup>2</sup> "Photo-chemical Investigations," *Journal of the Society of Chemical Industry*, 1890, 455.

<sup>3</sup> *Sitz. berichte der Wiener Akademie d. Wiss.*, Sect. 2A, 1899, or *Sensitometrie des plaques photographiques*, trad. par Ed. Belin, Gauthier-Villars, Paris (an English translation of this important work is much to be desired).

<sup>4</sup> *Eder's Jahrbuch f. Phot.*, 1896, 230, H. W. Vogel on "Sensitometry."

<sup>5</sup> J. Violle, *Comptes Rendus*, 122. 79; *Zeit. phys. Chem.*, 1896, 20. 613; but see also *Zeit. f. Beleuchtungswesen*, 1896, 384.

<sup>6</sup> V. B. Lewes, *Acetylene*.

<sup>7</sup> M. W. Travers, *Study of Gases*.



to a test-burner to ascertain the freedom of the gas from air, the other to the purifying apparatus and burner. These consisted in two purifiers containing caustic soda and bleaching powder,<sup>1</sup> then a large bottle with a manometer, and finally to the burner, which burnt  $\frac{1}{2}$  foot per hour, and was surrounded by a cylinder with a small aperture in front.

Subsequently we discovered that Dr. Meyer Wilderman was using, in the course of an investigation of "chemical statics and dynamics under the influence of light,"<sup>2</sup> an acetylene standard, in which the gas was produced in a Thorne and Hoddle "Incanto" generator, with a modified regulator for ensuring constancy of pressure within 1 per cent. Dr. Wilderman very kindly enabled us to inspect his apparatus for producing a constant light at the Davy-Faraday research laboratory, and we have adopted the Incanto generator as modified by him.

The gas, which is generated by water obtaining access to the carbide, then bubbles through the water in the gas-holder, and then through a special purifier, the pressure being registered by an oil-manometer.

The burners for low c.p. are as described before, the flame being completely enclosed and screened. For higher intensity a burner similar to that used by Dr. Wilderman is employed. This consists in a ring of small concentric jets, the burner being water-cooled, and the top of the flame cut off by an unadjustable screen, the flame being otherwise unscreened.

### *Sources of Error in Acetylene and Other Flame Burners.*

**Pressure.**—For gas-burners the constancy of pressure of the gas is the first desideratum; in the apparatus described this is obtained to 1 per cent. Further accuracy may be obtained if desired by the use of a balance-governor.<sup>3</sup> For screened burners very considerable modifications in the pressure

<sup>1</sup> V. B. Lewes, *loc. cit.*

<sup>2</sup> *Phil. Trans. Royal Soc., Zeit. phys. Chem.*

<sup>3</sup> Wilderman, *loc. cit.*

do not alter its intensity to any great extent, as the following table, obtained with our first apparatus, exhibits.

Pressures of 3, 4, 5, and 6.5 cms. of water.

D = density acc. to H. and D.

E = exposure in C.M.S.

E.	Log E.	D <sub>3</sub> .	D <sub>4</sub> .	D <sub>5</sub> .	D <sub>6.5</sub> .
209	2'321	1'226	1'330	1'233	1'16
106'1	2'026	1'037	1'163	1'018	1'040
53'2	1'725	0'844	0'973	0'896	0'850
27'9	1'446	0'609	0'760	0'651	0'655
19'98	1'114	0'373	0'508	0'464	0'468
7'65	0'884	—	0'298	0'286	0'293

From the curves—

P = 3 cms. Log i = 0.74	4 cms. 0.49	5 cms. 0.49	6.5 cms. 0.49
----------------------------	----------------	----------------	------------------

No change in the intensity is observable after 3 cms.

**Barometric Pressure and Composition of the Surrounding Atmosphere.**—It was noticed by Petavel<sup>1</sup> that the amount of moisture and CO<sub>2</sub> in the air had an appreciable effect on the amyl acetate lamp. This was confirmed by Liebenthal,<sup>2</sup> both for the amyl acetate lamp and the pentane standard; further, he noted the influence of the barometric pressure. Liebenthal found that errors of 8 per cent. might be caused in the Hefner lamp and 20 per cent. in the Pentane lamp. For the Hefner lamp he summarises his results in the formula—

$$I = 1.049(1 - 0.0053x)(1 - 0.00072x_1) + 0.00011(b - 760),$$

where  $I$  = light intensity.

$x$  = aqueous vapour per cubic metre.

$x_1 = \text{CO}_2$  „ „ (negligible in a large well-ventilated room).

$b$  = barometric height.

<sup>1</sup> *Eder's Jahrbuch f. Phot.*, 1901, 582.

<sup>2</sup> *Zeit. f. Instrumenten Kunde*, 1895, 15. 157.

It should be noticed, however, that Wilderman, using a sensitive Rubens thermopile to measure the intensity of his light, found it constant to 1 per cent. over long periods. He informs us that where greater accuracy than this is required the external conditions noticed above have to be considered. Further, it may be noted that, in burners completely enclosed such as we have employed, shortly after starting the air within the enclosure rapidly becomes saturated with moisture and  $\text{CO}_2$ , and assumes an equilibrium value which is practically constant, considering the small quantities outside. For screened burners the variation in barometric height is not important, as it only need be considered as a small variation of the total pressure.

**Temperature of Burner.**—One of the main sources of error with acetylene is the formation of polymers of acetylene by heating in the burner, which then choke it by depositing carbon. For small burners it is essential that the flame should never be turned down, but always used at its full intensity, and then cut right off. For larger burners the burner is water-cooled.

**The Exposure Instrument.**—Instruments for imposing a graduated series of exposures on a plate may be divided into two classes, according as they use an intensity scale or a time scale, *i.e.* they vary one factor of the expression  $IT$ , keeping the other constant. We will deal with the intensity scales first. Of these, one of the best known is the Warnerke sensitometer, which consists of a piece of glass covered with squares of pigmented gelatine, each square having an opaque number printed on it, and transmitting in each case  $\frac{1}{3}$  less light than the preceding. Another well-known scale is that of Spurge's sensitometer,<sup>1</sup> in which apertures of various sizes are used, each being, for example, increased by  $2\frac{1}{3}$ , so that every third hole doubles the light transmitted. A sensitometer of this form has also been employed by Dr. Vogel,<sup>2</sup> who has

<sup>1</sup> *Phot. Journ.*, 1881, 44; *ibid.*, 1885, 159; *ibid.*, 1887, 64; *Brit. Journ.*, 1881, 96 and 108; also *Journal of Camera Club*, 1893, 60.

<sup>2</sup> *Phot. Mitt*, 1895.

also employed paper intensity scales, in which increasing layers of paper are used.

Paper scales are only fit for rough measurements, as paper is in general an unstable material in light, and further may have unequal spectral absorption. An intensity scale (Rohr-photometer) used by Dr. Luther<sup>1</sup> consisted in a series of tubes, at one end of which was the plate, at the other a piece of paper with holes of various sizes cut out, this end being exposed to a uniform diffuse light. For a similar scale, see also Dr. H. W. Vogel.<sup>2</sup> A very useful intensity scale may easily be made by exposing a standard plate to a gradually increasing series of exposures, developing to a useful development factor, and then measuring the transparencies of the deposits with a photometer. If a non-staining developer be used, the intensities of the light transmitted can easily be calculated.

The chief general objection to intensity scales is the failure of the Bunsen-Roscoe "reciprocity" law,<sup>3</sup> according to which the "insolation" or exposure is equal to the product  $IT$ , where either factor may replace the other. Abney<sup>4</sup> and others have indicated departures from this law for photographic plates, so that at present an exact comparison of time and intensity scales over a long range is desirable.

*Time scales* may be impressed either by continuous or intermittent exposures. The former are for many reasons (*vide* later) the most desirable, but the latter are easiest to realise in practice. Thus Cowan<sup>5</sup> has proposed a form of drop shutter, with varying lengths of apertures, but this introduces an error due to gravity acceleration, which is difficult to compensate. The best form is that proposed by General Sebert

<sup>1</sup> "Umkehrbare photochemische Prozessen," *Zeit. phys. Chem.*, **30**, 628 (1899), and *Arch. Wiss. Phot.*, **2**, 35, 59 (1900).

<sup>2</sup> *Fortschritt. der Phot.*, 1883; *Eder's Handbuch*, **1A**, 412; *Vogel's Handbuch*, Bd. II, 51-53.

<sup>3</sup> *Pogg. Ann.*, **96**, 96 and 373; **100**, 43 and 481, 1855-1859; **101**, 255; **108**, 193.

<sup>4</sup> *Proc. Roy. Soc.*, 1893; Schwarzschild, *Eder's Jahrbuch*, 1899, 457.

<sup>5</sup> *Phot. Journ.*, 1887, 194 and 210; *Brit. Journ.*, 1880, 430.

at the Paris Congress, 1900.<sup>1</sup> In this the plate is passed at a definite rate by a clockwork mechanism before a number of slots of different lengths. Either this form, or one in which a band with increasing lengths cut out, and driven before the plate at a constant rate by clockwork, undoubtedly furnishes the best theoretical form of sensitometer.

A time scale with the exposure intermittent is easily given by a sector-wheel, *i.e.* a disc with successively increasing angular apertures cut out, as was proposed by Claudet in 1840 and W. B. Bolton;<sup>2</sup> this form was adopted by Hurter and Driffield in their well-known researches, and also by Scheiner<sup>3</sup> for his sensitometer. In Hurter and Driffield's form there are nine apertures, each angle from the centre being twice the preceding, while in Scheiner's the angular ratio is 1 : 1.27, which is convenient for measuring the Schwellenwerth or least visible exposure, but does not give the same range of exposure, as the Hurter and Driffield form does, on one plate.

The objections to the sector-wheel method of exposure are considerable. In the first place comes the difficulty of cutting the angles accurately; unless this is done with the precision of circle division, very large errors will be found in the smaller angles. The methods proposed by Hurter and Driffield<sup>4</sup> are entirely unsuitable for accurate work, and in any case the sectors should be subsequently calibrated. As the errors incidental to this method of exposure do not appear to have been noticed before, some details of the calibration of our first wheel may be of interest. This first wheel was made by dividing the brass disc by the sine method on a travelling micrometer, and then carefully filing out the angles marked. This filing was so well done that Mr. Holding cut his punch marks in half. The angles 180° and 90° were made by the 3, 4, 5 rule, and assumed correct; those of 45° and 22.5°

<sup>1</sup> *Eder's Jahrbuch*, 1902 : "Uhrwerk zur Messung der Empfindlichkeit photographischer Preparate."

<sup>2</sup> "Sensitometry" in *Phot. Journ.*, 1889, 809 and 840.

<sup>3</sup> "Universal Sensitometer," J. Scheiner in *Zeitschrift f. Instrumentenkunde*, 1894, 201; also Eder, "Sensitometrie des Plaques Photographiques."

<sup>4</sup> *Photo Miniature*, No. 56.

were checked by measuring the sines, the linear measurements being made with a Hilger travelling micrometer, kindly lent by Mr. E. C. C. Baly; for the smaller angles the wheel was set up before the Hüfner spectro-photometer, and driven by an electro-motor at such a speed that the "flicker" vanished; the differences in amounts of light transmitted were measured for successive pairs of angles, the results being given in the following table:—<sup>1</sup>

Angles of which difference was measured.	Ratio (a).	Ratio (b).	Mean.
0°75'–1°5'	0'438	0'437	0'4375
1°5'–3°	0'614	0'602	0'608
3°0'–6°0'	0'570	0'575	0'5725
6°0'–11°0'	0'4805	—	—
11°0'–22°	0'520	—	—

The accuracy of the above calibration is 1 in 176.

Angles measured by sines—

$$\begin{array}{ll} 45^{\circ}0' = 45^{\circ} & 48^{\circ}0' = 45^{\circ}8' \\ 22^{\circ}5' = 22^{\circ} & 59^{\circ}3' = 23^{\circ}0' \end{array}$$

TABLE.

	Aperture.	True aperture.	Ratio to 360°.
1	180°	180°	0'5
2	90°	90°	0'25
3	45°	45°8'	0'1275
4	22°5'	23°0'	0'0638
5	11°25'	11°96'	0'333
6	5°625'	5°575'	0'01549
7	2°812'	3°297'	0'00915
8	1°405'	2°003'	0'00556
9	0°703'	0°877'	0'002435

<sup>1</sup> This method, of course, assumes the validity of Talbot's law, according to which intermittent lightings integrate themselves by simple addition, and produce the same effect on the eye as the same exposure undivided. Talbot, *Phil. Mag.*, 1834, 321; Helmholtz, *Phys. Optik*, 339 (1st edition); also Section (4) on Photometry.

The last three angles show the errors that may occur for the small angles.<sup>1</sup>

Our second wheel was constructed by Messrs. Hilger with the greatest possible accuracy, and the error was less than that of the subsequent photometric calibration, *i.e.* less than 1 in 176. For picture, see Fig. 1.

It has been customary to rotate the sector-wheel in the photometer room in front of a dark slide containing the plate, but this method almost invariably causes trouble owing to reflections, etc., and is, moreover, very awkward to use, as it necessitates a dark room for exposure. We therefore mounted



FIG. 1.

our wheel in a guard-box (Figs. 2 and 3), 12 × 12 inches, at the back of which are fitted grooves, B, for the dark slide. The axis of the wheel, which is fitted with an adjustable cone bearing, has a number of pulleys, C, by means of which a varying speed can be obtained from the small hot-air engine used for driving. It is necessary that the wheel should be carefully balanced.

The dark slides are two in number, one taking two plates  $4\frac{1}{4} \times 1$  inches, and the other one plate  $4\frac{1}{4} \times 1\frac{1}{2}$  inches; this last has two shutters, so that two series of exposures can be

<sup>1</sup> For intermittency error, see p. 222.

impressed on one plate. In both slides only a narrow strip  $\frac{3}{8}$  inch in width is exposed, a fog strip being reserved as described in the discussion of the photometer.

This guard-box fits on to a camera,  $4 \times 4 \times 12$  inches, D. This contains a flap shutter, E, for making the exposures and grooves, F, for two fluid cells, by which monochromatic light

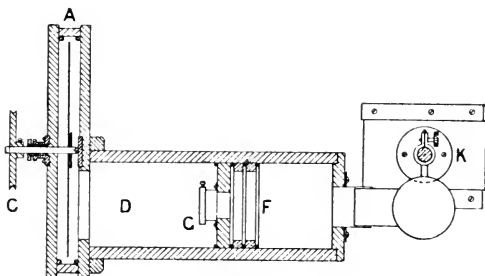


FIG. 2.

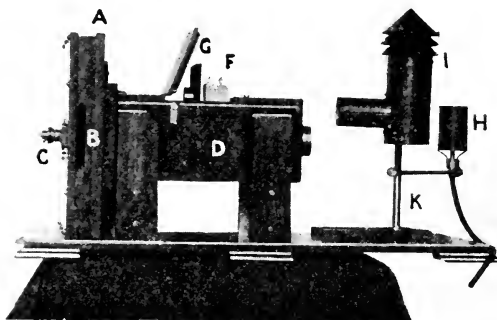


FIG. 3.

of any colour can be obtained. In working at commercial speed-finding, the box is fitted with a light blue screen, so that the spectral composition of the acetylene light used is reduced to be almost exactly the same as daylight, in order that orthochromatic plates may give numbers, which in regard to ordinary plates represent fairly their relative



behaviour to midday cloud-light. Most orthochromatic plates give much too high speed numbers when these numbers are found in the ordinary way.

The acetylene burner, H, previously described, is mounted on a stand, K, with a universal movement, and enclosed in a light-tight but well-ventilated cylinder with hood, I: this fits on to the front of the camera. Since the burner is only a short distance, about  $\frac{1}{2}$  mètre, from the plate, it is necessary to add a correction to the exposure scale for the error due to the angle of incidence.

We owe our best thanks to Mr. J. F. Holding, of University College, for the painstaking care which he has expended in the construction of these exposure instruments.

#### *A Developing Instrument for the Control of Temperature during Development.*

In order to attain accurate results, either in researches on the phenomena of development or in sensitometric measurements as to the developing properties of a plate, it is necessary that some method by which developer, plates, etc., may be maintained at a constant temperature should be devised. This may be done, as Mr. Driffeld has pointed out,<sup>1</sup> by means of large baths of warm water in which the developing dishes rest, but it is very much more satisfactory to arrange a proper thermostat for development in the method now described.

A thermostat consists of a large body of water in continuous circulation by means of a stirrer, and maintained at a constant temperature by means of a heat source regulated by an automatic, usually mercury, regulator. For a very complete discussion of thermostats, see Ostwald-Luther, *Physico-Chemische Messungen*.

In order to attain constancy of results it is, of course, necessary that the developer should be maintained in some regular movement, and as it is quite impracticable to do this

<sup>1</sup> *Phot. Journ.*, January, 1903.

in a flat dish in any simple manner (though we have devised a method of using flat dishes on a large scale), it was decided to develop the plates in an upright position by rotating them in vertical tubes.

In the course of our earlier work we had exceedingly great trouble in avoiding the continuous and heavy fog which occurred, and therefore give the following list of conditions for avoiding fog :—

(1) The burnt gas from the heating burner must not enter the dark room at all.

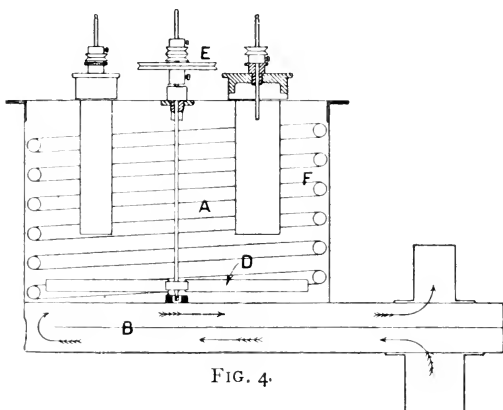


FIG. 4.

(2) It must be impossible for any vapour from the water in the thermostat to reach the plates.

(3) No zinc or lead whatever must be used in the thermostat except as solder, where the proportion is insufficient to cause trouble.

(4) The tubes containing the developer must be of glass, and must have light-tight covers.

(5) The holders for the plates must be of xylonite. This is the only substance we have found practicable; of course glass would do, and so probably would silver or platinum, but xylonite is far simpler.

(6) The speed of rotation must be quite low, thirty rotations a minute is quite sufficient.

In this thermostat all these conditions will be seen to be fulfilled. This type was designed by Mr. A. D. Cowper, F.C.S., of University College, from our suggestions, and was made by Mr. J. F. Holding, the laboratory mechanic, to whom we owe our best thanks.

The thermostat consists of a large copper box, tinned inside, A (Fig. 4), containing about 10 gallons of water, and mounted on a second box, B, which forms the heating apparatus. This second box is arranged so that the hot gases from the burner pass under the base of the thermostat, and thence through a long flue, C (Fig. 5), into the outer air. This second box is made so that it can be passed through the wall of the dark room, so that the burner and long flues are in the outer laboratory. The gas for the burner passes first through the mercury regulator, which is of the ordinary Reichart type, and then through the wall to the burner, so that the burner is governed by the regulator in the thermostat.

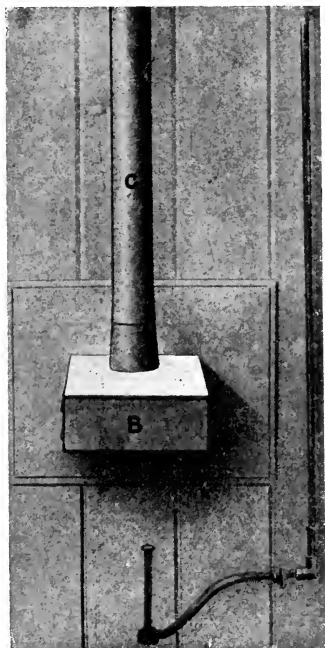


FIG. 5.—Flues in outer laboratory.

The circulation of the water is ensured by means of a large four-bladed stirrer, D (Fig. 4), which has a point and cup bearing at the bottom of the thermostat, and which also passes through the lid of the instrument being driven by means of a pulley, E, from a source of power. On the shaft of this stirrer

there are also other pulleys mounted, by which the plates may be rotated.

A very large coil of composition piping, F (Fig. 4), passes entirely round the inside of the thermostat, so that cold water may easily be made to circulate round the instrument for cooling purposes; filling and emptying taps and a water-gauge are also provided, while the lid has holes

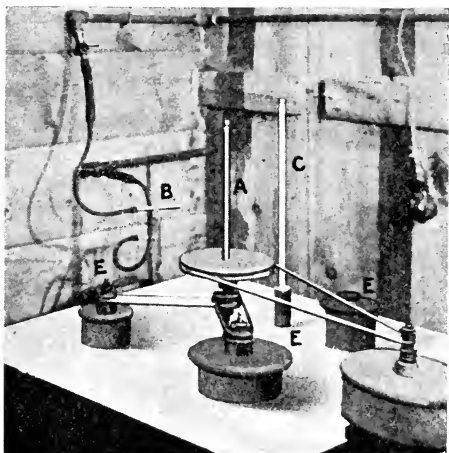


FIG. 6.—*Top of thermostat in dark room.*

A. Central stirrer.

B. Thermo regulator.

C. Thermometer.

E. Top of developing pots.

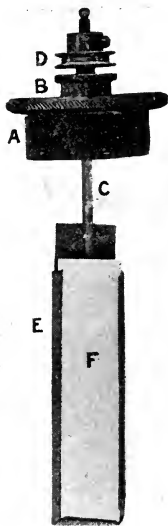


FIG. 7.

for filler, for the regulator, and for a thermometer divided to  $\frac{1}{10}$  C.

In the lid, which is a close-fitting one, there are placed tubes of brass, which project into the water and which are of two sizes, corresponding to the two sizes of plates used (Fig. 7).

These brass tubes allow glass tubes to be slid down into them which contain the developing solutions.

It is found that for the  $4\frac{1}{4} \times 1$  inch plates, a tube requiring

100 c.c. of developer must be used, while for the  $4\frac{1}{4} \times 1\frac{1}{2}$  inch plates 200 c.c. will be necessary.

Into the tops of these brass tubes vulcanite covers, A, are fitted (Fig. 7), having a brass bearing, B, taking a spindle, C, split at the bottom, and carrying a small pulley above.

Into the split of this spindle is pushed the xylonite plate-holder E, which consists of a sheet of xylonite turned over at the bottom and sides (by the aid of hot water), and into which the plate F can be slipped from above before it is pushed into the split.

It is convenient to have both narrow and wide splits in the spindle, so that either one plate-holder can be used or two placed back to back. A plate-holder with very shallow sides is also useful, so that the plate can be very quickly jerked out when pairs of plates are being developed together, one for a longer time than the other.

The best form of belt for driving the small plate pulleys from the central pulley is a continuous round rubber band; all the small pulleys should be arranged at the same distance from the central pulley, as is shown in Fig. 7.

The procedure of development is as follows:—One tube is filled with distilled water and the other with the developer,<sup>1</sup> and they are left for twenty minutes to assume the temperature of the thermostat (our standard is  $20^{\circ}\text{C}$ ). At the expiration of this time the plate is placed in its holder, which is then inserted in its split spindle, and is rotated in the distilled water for two minutes, after which it is rotated in the developer for the desired time, again in the distilled water for one minute, and then fixed.

A small electric light covered with red fabric is a very great convenience when working at the thermostat.

All timing should be done with a stop-watch, and it is advisable to reserve a watch for the purpose, as the work is very heavy for it.

<sup>1</sup> For our standard developer, see *Photographic Journal*, July, 1903.

## PHOTOMETERS.

Photometers may be divided into two classes, according to the purposes they have to serve: firstly, "bench photometers," for the purpose of comparing the intensities of light sources, many forms of which have been evolved during the progress of lighting technology, and which it is not proposed to discuss here;<sup>1</sup> secondly, those intended for the measurement of the absorption of light by various media.

Now, in surveying this class of instrument with a view of obtaining one for photographic measurements, it became obvious that the instruments devised in England for density measurement were generally only modified "bench photometers," and that the most efficient form of absorption photometer was that used for physiological and physico-chemical investigations. We may divide, for purposes of discussion, photometers for absorption work into the following classes:—

(a) Modified bench photometers.

(β) Micro-photometers.

(γ) Spectro-photometers.

(δ) Automatic photometers, *i.e.* those in which the registration is effected by some sensitive instrument, as the bolometer, etc.

(a) As mentioned above, the first class given here have been generally used in England for measurements of the density of photographic plates. Thus, in 1877 Captain Abney used a Rumford screen as an indicator and cut down the light with a rotating sector. He has improved his method at various times;<sup>2</sup> also used a blackened wedge for diminishing the intensity. A criticism of his method by Hurter and Driffield attacked both the use of a white-paper screen and of

<sup>1</sup> See any standard work on Photometry, *e.g.* J. Dibden, *Photometry*.

<sup>2</sup> *Eder's Jahrbuch*, 1881, 461; see also note by Dr. Stolz. Abney, "Notes on Sensitometry," *Brit. Journ.*, 1882, 243. Abney, "On Measuring Densities of Photographic Plates," *Phot. Journ.*, 1887, 38; Abney, 1887, 64. Abney, *Journal of the Camera Club*, 4. 191; also *Instruction in Photography*, W. de W. Abney.

the revolving sector.<sup>1</sup> A further modification of Abney's method, involving the use of one light source, was made by Chapman Jones in his Opacity meter.<sup>2</sup>

Instead of the Rumford shadow indicator the Bunsen grease-spot may be used, and this was adopted for their well-known photometer by Hurter and Driffield.<sup>3</sup>

Generally it may be objected that all these forms are clumsy and comparatively inaccurate (3 to 7 per cent.); neither of the above methods are used in accurate bench photometry now, and the use of two light sources involves an unnecessary source of error. For a discussion of the principles of photometry, and especially on the value of the rotating sector, the classical articles of Lummer and Brodhun should be consulted.<sup>4</sup>

References to photometers and spectro-photometers using the Lummer-Brodhun head as indicator will be found in the bibliography.

Simmance and Abady's new flicker photometer possibly forms the best of the bench photometer heads, but has not yet been applied to the measurement of photographic plates.<sup>5</sup>

( $\beta$ ) Photometers using the microscope demand some notice, as they have been used for photographic measurements, notably by Dr. J. M. Eder,<sup>6</sup> who used the Hartmann instrument. In this, two microscopic objectives are used, the fields being brought together by a Lummer-Brodhun head; the central field is filled by a standard density from a graded scale, the outer by the density to be measured; any error in the original standard would vitiate the other measurements, while, as the

<sup>1</sup> *Journal of the Society of Chemical Industry*, 1890, **X**. 725; *ibid.*, Abney, 722; also *ibid.*, Hurter and Driffield, 1891, **XI**. 98.

<sup>2</sup> *Phot. Journ.*, 1895.

<sup>3</sup> *Journal of the Society of Chemical Industry*, 1890, **X**. 455; cf. also *Photo Miniature*, **V**. No. 56, pp. 368 *et seq.* "Criticisms," by Abney, *vide supra*; also *J.C.S.I.*, 1891, 18, and reply by H. and D., 20.

<sup>4</sup> *Zeit. f. Instrumentenkunde*, 1889, **9**. 41 and 61; 1890, **10**. 119; 1892, **12**. 41; and 1896, **16**. 299.

<sup>5</sup> Simmance and Abady, *Philosophical Magazine*, 1904, April.

<sup>6</sup> *Système de sensitométrie des plaques photographiques*, trad. par Ed. Belin, 14; *Eder's Jahrbuch*, 1899, 106.

scale is discontinuous, a very close number of steps is necessary; no measurements exhibiting the accuracy of the instrument are given.

J. Koenigsberger<sup>1</sup> has designed a micro-photometer with some novel points; it consists of a polarisation microscope, before the objective of which is an Iceland spar plate and a double prism of the Thompson type, so that the extraordinary image of one opening lies next to the ordinary image of the other; the interference phenomena of a Savart plate are used to equate the contrast, the diminution of the light intensity being made by means of a second Thompson polarisation prism.

One objection to micro-photometers for photographic work is the small area of deposit covered; although this may be an advantage for some work, as in stellar photometry, it is hardly so for sensitometry, where small local deviations in the plates would cause errors.

( $\gamma$ ) **Differential Spectro-photometers.**—These are the forms which have been evolved for physiological and physico-chemical investigation.<sup>2</sup> Two portions of a spectroscopic slit, illuminated by one light source, are brought into optical contact<sup>3</sup> by some prism device. The intensity of one-half of the slit is diminished by the absorption to be measured, that of the other in some measurable manner, as by means of a closing slit (Vierordt) or by polarising prisms (Zöllner, Glan, Hüfner, etc.).

The best optical device for bringing the two fields into contact is probably the Hüfner-Albrecht rhomb,<sup>4</sup> and the Hüfner spectro-photometer, with several modifications, is the instrument we have adopted (Fig. 8). One Welsbach burner,

<sup>1</sup> *Zeit. f. Instrumentenkunde*, 1901, Bd. 21. 129; and Spectroscope addition, *ibid.*, 1902, Bd. 22. 129.

<sup>2</sup> For a general discussion of the instruments and methods of spectro-photometry, see Ostwald-Luther, *Physico-Chemische Messungen*, and G. and H. Krüss, *Quantitative Kolorimetrie und Spectrophotometrie*.

<sup>3</sup> The whole basis of photometry rests on obtaining the two fields to be compared in as close contact as possible, so as to use to the utmost the eye's power of perceiving contrast.

<sup>4</sup> *Zeit. phys. Chem.*, III. 562 ff, and see later for figure.



A (Figs. 8 and 9), is used, and the light from this passes through a Hñfner-Albrecht rhomb, B, before it reaches the slit

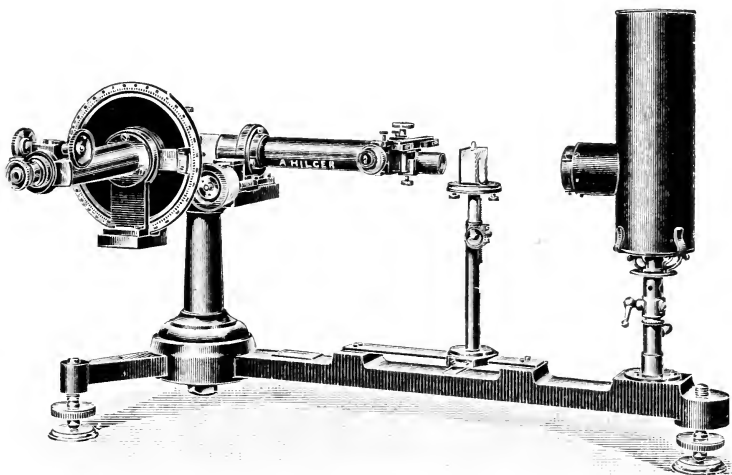


FIG. 8.

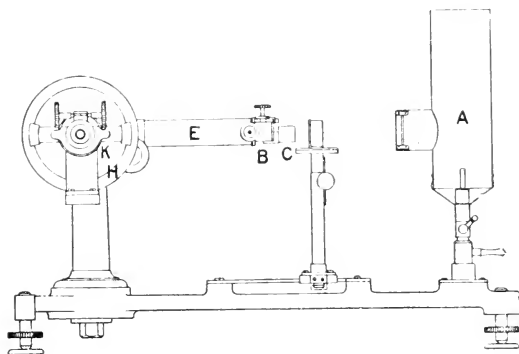


FIG. 9.

of the spectroscope. Before the lower half of the Albrecht rhomb is placed, a small polarising nicol, C, and the absorption to be measured occludes the upper half; moreover, before the

upper half there can be moved by a graduated rack adjustment a smoke glass wedge, which allows the absorption due to the polarising prisms being compensated. It is clear that at the slit we shall have two fields in contact, the upper one being polarised (the positions of the fields are reversed by the prism), but otherwise undiminished, the lower one being diminished by the absorption to be measured. After passing through the collimator, E, and dispersion prism, F, the rays forming both fields pass through an analysing nicol, G, which can be rotated on its axis, the rotation being measured by a divided circle, H, with a vernier. They then pass through the telescope of the spectroscope, the fields being again optically reversed in position, so that the field diminished by the absorption to be measured is again uppermost.

To make measurements, after setting the nicols accurately parallel, the circle of the analyser is set at zero, and the slight absorption due to the nicols is adjusted by means of the smoked glass wedge. The absorption to be measured is placed in front of the upper portion of the slit, and the intensity of the unchanged field altered by means of the analyser till both fields are equal in brightness.

Further, it may be mentioned that for density measurements, where densities ranging greatly in magnitude are in question, the intensity of the total light employed may be adjusted by means of the spectroscope slit, so that the most favourable intensity of field may be used. This intensity, which varies for different observers, is easily found after a little practice.

### *Numerical Expression of the Results.*

The intensity of light passing through crossed nicols is proportional to the square of the cosine of the angle between them—

$$\text{i.e. } T = \text{transparency} = \cos^2 \theta$$

$$O = \text{opacity} = \frac{1}{\cos^2 \theta}$$

$$\text{and } D = \text{density} = -\log_{10} \cos^2 \theta$$

if Hurter and Driffeld's notation be used.<sup>1</sup>

<sup>1</sup> Vide also Luther, *Zeit. phys. Chem.*, 1900, **33**. 252.

It follows that the error in density for any error given in the angle of rotation is—

$$\frac{dD}{d\theta} = \frac{d(-\log \cos^2 \theta)}{d\theta} = 2 \tan \theta$$

therefore the proportionate error is—

$$\frac{dD}{D} = \frac{-2 \tan \theta d\theta}{\log \cos^2 \theta}$$

In use a corresponding table of values of  $D = -\log \cos^2 \theta$ , and  $\theta$ , the angle of rotation, is constructed.

### *The Instrument as a Spectro-photometer.*

Although in general monochromatic light is not essential for measurements of densities of photographic plates, yet so many and various are the spectroscopic measurements in photographic science that the spectral adjustments of the instrument constitute a most useful and important feature. We shall here describe the optical arrangements in the Hüfner photometer as modified by ourselves, and constructed and designed by Messrs. A. Hilger, to whose manager, Mr. Twyman, we should here like to express our great indebtedness for the interest and ability he has displayed in this work.

**The Slit** is of the usual type adopted in accurate spectroscopes, the breadth being indicated on the drum of a micrometer screw. As before explained, this plays an important part in density measurements by regulating the intensity of the field used.

**The Dispersion Prism.**—In the former type of instrument the usual prism set at minimum deviation was used, and the movement through the spectrum obtained by rotating the spectroscope telescope round the axis of the prism. The position of field in the spectrum is indicated by a pointer moving round an arc of a divided circle. In the improved form Hilger's constant deviation prism (*vide* Fig. 11) is used, which is itself rotated, the telescope being fixed at right angles to the collimator. This prism may be considered as

built up of two  $30^\circ$  prisms and one right-angle prism, from the hypotenuse of which light is internally reflected, as shown in diagram. The prism is, however, made in one piece. The collimator and telescope are permanently fixed at right angles to each other, and the portion of the spectrum in the middle of the field of view of the telescope is then seen subjected to a dispersion equal to that of a  $60^\circ$  prism fixed for minimum deviation for that particular part of the spectrum. The passing from one part of the spectrum to the other is effected by rotation of the prism, and it is to be noted that the above statement concerning the dispersion is true *for each portion of*

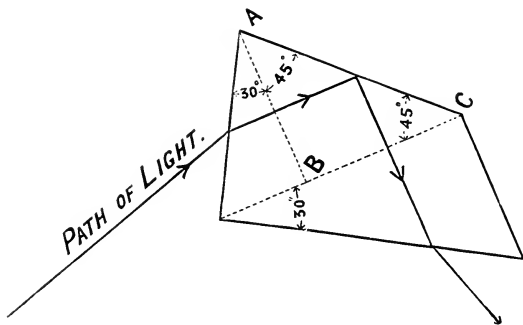


FIG. 10.

*the spectrum as it comes into the middle of the field.* The readings are given direct in wave-lengths on the drum of the actuating gear. (See later under *Wave-length Determinations.*)

**The Ocular Slit.**—In order to isolate any desired portion of the spectral field, there is an adjustment in front of the ocular of the telescope. This consists of two leaves sliding in a groove, the edges being slightly curved to fit the curve of a spectral line due to the prismatic distortion. On the groove above is a scale so that the distance between the leaves can be read (K, Fig. 9). This scale is calibrated in wave-lengths in a manner described subsequently.

**Spectro-photometric Trough.**—For measuring the absorption of fluids, a small Schulze cell is used, made of optically plane glass. The thickness of the cell is 11 mm. If a Schulze-körper, which is a piece of homogeneous optically worked glass, is placed below so as to fill 10 mm. of the cell, we can then measure the absorption due to a layer of 10 mm. of the fluid. If a Schulze-körper of 11 mm., which completely fills the cell, be placed below, and a 10-mm. thick body above, we have a layer 1 mm. thick.

### Spectroscopic Measurements :—

*Wave-lengths.*—The instrument may be used to determine wave-lengths direct to 10 Ångström units.

*Absorption Spectra.*—Both the breadth of absorption bands and the extent of the absorption throughout the spectrum are conveniently measured. The use of this for colour screens, etc., is obvious.

*Calibration of the Ocular Slit.*—This is done by adjusting a spectrum line (Na, *e.g.*) on the edge of the right-hand sheath when fixed at zero, and then moving the edge of the sheath through the scale for a desired distance, and again adjusting the spectral line. The corresponding values of the ocular and wave-length scales, which should be obtained for different parts of the spectrum, enable the calibration table to be constructed.

The essentials in accurate spectro-photometric measurements are a pure spectrum,<sup>1</sup> and as narrow an ocular slit as possible.<sup>2</sup>

Other spectro-photometers based on similar principles are those of Glan, Gouy, and König, already referred to.

An important modification adopted by Dr. H. Simon allows spectro-photometric measurements to be prolonged into the ultra-violet. This consists in placing before the ocular an

<sup>1</sup> On the relation between the purity of spectrum and breadth of collimator slit, *vide Encyclopædia Britannica*, art. "Spectroscopy," 10th edit.

<sup>2</sup> For a very complete discussion of spectro-photometry and the sources of error, see Martens, "A New Form of König's Spectro-photometer" : *Drude's Annalen d. physik u. Chemie*, 1903.

arrangement for photographing the spectrum, and subsequently measuring its density.<sup>1</sup>

**Automatic Photometers.**—A photometer independent of the eye and physiological and psychological sources of error, is naturally the one most to be desired for accurate work; but, unfortunately, at present no satisfactory substitute has been found. So far there have been used the selenium cell, the thermopile or bolometer, and, for ultra-violet light, the rate of discharge of an electroscope by a polished metal surface. Of these the thermopile has, so far, proved the most satisfactory, and may probably be adopted, as it can be used even into the ultra-violet.<sup>2</sup> For general references, see bibliography.

### *The Carriers for the Spectro-photometer Front.*

Inasmuch as the Hüfner spectro-photometer had not before been used for measuring the densities of photographic plates, it was necessary that we should work out a convenient holder for isolating the patch to be measured.

Three different types of fronts have now been devised by us which fit on the top of the sliding pillar in place of the holder for the Schulze cell.

With these three fronts we can—

- (1) Measure the densities of sensitometric plates.
- (2) Compare the intensities throughout the spectrum of two light sources.
- (3) Measure the reflecting power of surfaces, *e.g.* the surface of photographic plates,<sup>3</sup> for any portion of the spectrum.

We have also designed an addition to the photometer front for the measurement of very high densities, while if we place a pair of  $30^\circ$  prisms along the faces of the constant deviation prism, we obtain a simple reflecting prism without dispersion, by means of which the photometer can be used for all the above purposes for heterogeneous light instead of

<sup>1</sup> *Eder's Jahrbuch*, 1879, 38; 1898, 10.

<sup>2</sup> *Zeit. f. wiss. Phot.*, Bd. I.

<sup>3</sup> The description of these is not given as they are not germane to the major portion of this treatise. See, however, *Roy. Phot. Journ.*, July, 1904.

spectrum light, *e.g.* it can be used as an ordinary photometer for comparing luminosities.

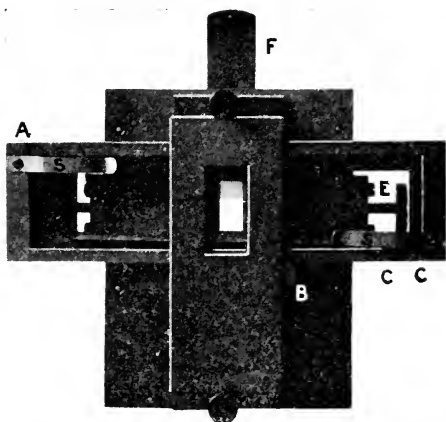


FIG. 11.

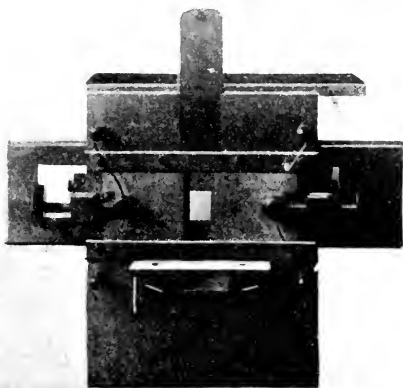


FIG. 12.

Fitting for measuring the densities of sensitometric plates (Figs. 11 and 12).

The plates are fixed by little springs into a carrier, A,

which slides through another carrier having a spring pointer, B, clicking into a series of nine slits (C, C) placed  $\frac{2}{5}$  inch apart to correspond with the series of densities impressed upon the plate during exposure.

This carrier is then adjusted upon a face plate before a rectangular opening, the side of which can be adjusted by means of small shutters, D, D, regulated by fine screws, E, E, and from above by means of a push-down shutter, F. When one density is in position, all will be right with regard to their own slots. It is advisable to cut away 4 inches in the carrier so as to give  $\frac{2}{5}$  inch beyond the densities themselves for adjusting the compensating wedge of the spectro-photometer with the analyser at  $0^\circ$ . This allows this adjustment to be done with the plate in position.

It is necessary to have two sizes in these carriers, one for the 1-inch plate and the other for the  $1\frac{1}{2}$ -inch; that for the  $1\frac{1}{2}$ -inch must be made reversible.

Now, in measurements of plates, it is usually necessary to measure very high densities, but it is exceedingly difficult to make an instrument in which scattered and elliptically polarised light is less than  $\frac{1}{10000}$  of the incident beam, and yet this amount would produce an error of 3 per cent. on a density of 3.

We have, therefore, adopted the simple but exceedingly useful plan of placing over the front nicol a cap containing a piece of worked neutral tint, having a density very accurately measured of about 2.0.

With high densities this cap is slipped on, and its density added to that calculated from the angular reading. This enables us to measure to about 4.5.

In plotting the curves of plates, it was the practice of Messrs. Hurter and Driffeld to measure the density of unexposed portions of the plate, and to subtract this throughout from the measured density. Dr. Eder adopts the same method.

Since our photometer is a differential one, we so arranged our dark slides in the exposure machine as to give an unexposed strip of plate alongside the graduated strip of densities,



and this unexposed strip is used as the comparison clear glass. The fog strip is thus automatically compensated, and is taken from the adjacent portion of the emulsion to the exposed density.

All densities are measured in the bright green (position of maximum visual luminosity), but the opacity of unexposed plates is measured for the blue-violet position of maximum sensitiveness.

*On the Probable Error in working the Spectro-photometer.*

The following method of calculating the spectro-photometer error was kindly suggested by Dr. L. N. G. Filon, of University College.

Four readings being taken, the differences between every pair are taken and the mean difference is found. The value is approximately the same as the error of mean square, and the method does not require an accurate knowledge of the true mean, and can therefore be used for small numbers of readings.

$\frac{1}{\sqrt{2}}$  times this value will be the probable error (the scatter) for a single reading.

Thus if mean angle be  $84.3$ .

$$D = -\log \cos^2 \theta = 2.01.$$

readings be  $84.4 \quad . \quad 84.4 \quad . \quad 83.9 \quad . \quad 84.4$ .

densities  $2.022 \quad . \quad 2.022 \quad . \quad 1.948 \quad . \quad 2.022$ .

$\Delta \quad 0.074 \quad . \quad 0.074 \quad . \quad 0.074 \quad . \quad \text{Mean } \Delta = 0.037$ .

P.E. =  $0.026$ .

Percentage P.E.  $1.27$ .

Around each density four sets of readings were selected at random for the purpose of calculating the probable error.

Thus around  $D = 1.640$  we have:—

Density.	P.E. percentage.
1.640	0.43
1.680	0.39
1.630	0.52
1.630	0.67
Mean 0.50 per cent.	

In this way the following results were obtained :—

Density.	P.E.	P.E. percentage.
1·645	0·0082	0·50
1·380	0·0097	0·70
1·190	0·00475	0·40
0·940	0·0068	0·68
0·690	0·00468	0·68
0·490	0·00495	1·01
0·390	0·00825	2·11
0·125	0·00592	4·73

These numbers give some idea of the percentage P.E. for a single reading.

They may be regarded as the greatest P.E.'s likely to be obtained, as they were taken under unfavourable conditions; frequently the accuracy is much greater.

If more than one reading is taken, the P.E. will vary inversely as the square-root of the number of readings taken.

For a bibliography of this subject, see *Phot. Journ.*, July, 1904.

**Relation of Density to Mass of Silver.**—The next consideration is as to how far  $D$  represents the mass of silver per unit area. In treating the image as obeying the absorption law, no account is taken of the light diffusely scattered.<sup>1</sup> It is true that so long as all densities are measured at the same distance, the scattered light lost is probably proportional to the scattering surface, *i.e.* to the density. In this case the result does not affect the form of the curve, for  $D = \phi(T) = \phi'(\text{mass of silver})$ , but only the slope, *i.e.* the photometer-constant. But the error due to this cause with the Hüfner instrument is, for negatives, inappreciable. If proper precautions with regard to obstruction of light by the absorption stand are taken, and adjustment made so that the zero does not alter, it is found that the measured density does not alter on changing the distance of the light source. Further, if a diffusing medium, such as milk-glass, be interposed, the density

<sup>1</sup> Abney, *Phil. Mag.*, 1875; C. Jones, *Phot. Journ.*, 1898-1899, 99.

readings are not altered beyond the probable error. On the other hand, if this be done with an undeveloped plate, quite different readings are obtained. When measuring highly diffusing media, such as haloid of silver emulsions, *it is necessary to use a highly diffusing light source, and also to utilize only a narrow strip of the transmitted bundle of rays.* This may be accomplished by means of the carriers described on p. 36.

**The Photometric Constant.**—Hurter and Driffeld showed that the amount of silver per unit area was directly proportional to the density  $D = -\log T$ , where  $T$  is the photometric transparency. This was found for densities from 0.525 to 2.0, the mean value of  $P$  being 0.0121.  $P$  is the mass of silver in grammes per 100 cms.<sup>2</sup>, corresponding to a density of 1.0, and is henceforth referred to as the photometric constant. A redetermination of  $P$  in 1898 gave  $P = 0.0131$  for ferrous oxalate. The photometric constant varies slightly with the developer, especially if organic stain be deposited. Dr. Eder also confirmed this ratio for densities from 0.5 to 2.0, and obtained the value 0.0103 for  $P$  (ferrous oxalate). As this relation is of great importance in the theory of development and sensitometry, we made a redetermination, extending the range of densities to 3.5, as it seemed possible divergencies might occur at higher densities. The photometric constant allows quantities of silver to be estimated much below analytical measurement.

Hurter and Driffeld, after the necessary density-measurements, removed the film from the plate and dissolved the silver in nitric acid: it was then precipitated as  $\text{AgCl}$ , and weighed. Dr. Eder converted the silver directly by means of bichromate and  $\text{HCl}$  into  $\text{AgCl}$ .

These gravimetric methods are somewhat disadvantageous in dealing with the small quantities of silver present. If plates of small area are used, the ultimate analytical error for so small a quantity of  $\text{AgCl}$  may seriously affect the results, while with larger plates the irregularity in the developed density, primarily due to coating, causes errors which are only partially compensated by taking many readings over the plate. It

would be preferable, moreover, to precipitate the silver as AgBr, both owing to its slighter solubility and the greater weight of precipitate obtained.

A preliminary gravimetric determination was made, in order to check the volumetric method subsequently employed. The densities ranged from 2.4 to 3.25, and the value of P obtained was 0.01035.

The volumetric method adopted was Volhard's,<sup>1</sup> with thiocyanate, sometimes controlled by the precipitation with KBr. The standard silver solution was N/100 AgNO<sub>3</sub>, prepared by dissolving 1.6997 grammes pure AgNO<sub>3</sub> in water with excess of HNO<sub>3</sub>, and made up to 1000 c.c. at 15° C. This was checked by analysis, and two concordant determinations gave the factor 1.001. The standard KCNS N/100 had the factor 1.017.

**Details of the Estimation on Plates.**—Half-plates and whole-plates were exposed at 2 to 3 metres, carefully developed, fixed, and washed. Very careful washing was necessary in order to extract all soluble salts. They were dried at the standard temperature. The density was measured in 20 to 30 places,<sup>2</sup> and the area; after this the film was removed by dilute HF and soaked in many changes of distilled water, with frequent pressure between filter paper, to remove all soluble salts which might interfere.<sup>3</sup> The film was then dissolved in slight excess of pure HNO<sub>3</sub>, S.G. 1.49, and the gelatine completely destroyed by heating, as otherwise it interferes with the subsequent titration by forming a pseudo-solution of the precipitate and retarding its aggregation.<sup>4</sup> The solution was made up to 25 c.c. at 15° C., and titrated with N/100 KCNS, using 2 c.c. of 10 per cent. ferric-am. sulphate as indicator.

The following series is exemplary. Four series of measurements were made in this way, the density ranging from 0.50

<sup>1</sup> Cf. Mohr's *Titrimethode*.

<sup>2</sup> This was necessary, as variations in the developed density up to 10 per cent. occurred, chiefly due to coating errors.

<sup>3</sup> Cf. Lumière and Seyewetz "On Retention of Hypo," ref. in *Phot. Journ.*, 1902.

<sup>4</sup> Lobry de Bruyn, *Ber.*, 1902, **35**. 3079-3082.

to 3.5, and the curve shows that there is no bias throughout the range.

#### SERIES IV.

Plate.	Area.	Density.	Titre.	P.
1	87.2 cms. <sup>2</sup>	1.438	11.8 c.c.	0.01033
3	86.7 "	2.392	18.7 "	0.01019
4	87.2 "	2.067	16.5 "	0.01032
5	87.2 "	1.809	14.95 "	0.01040
6	87.2 "	1.618	13.1 "	0.01022

The means of all series are as follows:—

I.	. . . . .	0.01035	gravimetric
II.	. . . . .	0.01012	volumetric
III.	. . . . .	0.01037	"
IV.	. . . . .	0.01029	"
V.	. . . . .	0.01040	"
Total mean	. . . . .	0.01031	= P for plates employed

Wratten ordinary emulsion and ferrous oxalate. Curve I. shows the directly proportional ratio between the density  $D = \log_{10} O$  and the mass of silver per 100 cms.<sup>2</sup>. The mean value differs materially from that found by Hurter and Driffeld, but this may be due (*a*) to a constant error in their photometer; (*b*) to the plates used, as it seems probable that the emulsification of the silver haloid has considerable influence on the "covering power" of the silver subsequently deposited. This "covering power" is, of course, the quantity P, or photometric constant.

The extent to which the exponential law holds for gelatine emulsions is of great practical importance, as it provides a rapid and easy method of measuring the amount of substance present. The following experiments indicate that it holds within certain limits:—

TABLE CALCULATED FROM HURTER AND DRIFFIELD.

Plate.	AgBr per 100 cms. <sup>2</sup> .	Density.
1	0.016 gramme	0.240
2	0.031 „	0.520
3	0.062 „	1.000
4	0.124 „	2.900

The writers converted silver into AgBr and measured the density in each case. Considering how high the figures are, the results are satisfactory.

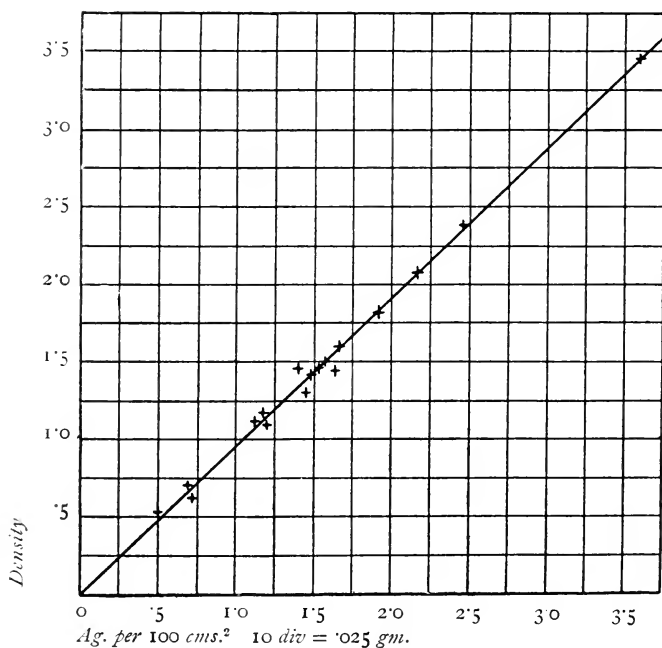


FIG. 13.

## SERIES I.

Density of silver, 2.023 }  
 „ AgBr, 4.020 } P, for AgBr = 0.0364

## SERIES II.

Density of silver, 1.009 }  
 „ AgBr, 2.026 } P, for AgBr = 0.0393

Comparing these with Hurter and Driffeld's numbers, it is obvious that the physical state of the haloid has tremendous influence on the opacity. Considering the importance of this quantity for sensitometry, the constant P seems worthy of investigation in connection with emulsification.

The investigation shows that the density can be accepted as a measure of the mass of silver reduced.

## PART II

### *THE PHYSICAL CHEMISTRY OF EXPOSURE, DEVELOPMENT, AND FIXATION*

#### CHAPTER I

#### THE CHEMICAL DYNAMICS OF DEVELOPMENT WITH IRON SALTS

**Historical and Introductory.**—The following work was undertaken with the view of applying physico-chemical methods to the study of photographic development. Although, as has been pointed out by Ostwald, the problem falls in the province of chemical dynamics, but little systematic work has been done from this point of view. The increasing use of gelatino-bromide films in connection with radiation phenomena make a greater knowledge of the laws describing development and exposure very desirable, while the importance of the photographic industry needs no comment. The following brief historical introduction is necessary in order to sum up the progress made and the terminology in use :—

In 1878, Sir W. Abney<sup>1</sup> showed that the black reduction product in development was metallic silver. He introduced the measurement of the transparency of the deposits by means of a photometer, and proposed as the relation between the mass of silver reduced and the transparency a form of the law of error. In 1890, Messrs. F. Hurter and V. C. Driffield<sup>2</sup>

<sup>1</sup> *Phil. Mag.*, 1878 ; also *Encyc. Britt.*, 10th edit., art. "Photography."

<sup>2</sup> *Journ. of Soc. of Chem. Industry*, May, 1890.



made a systematic survey of exposure and development in which a new terminology was introduced and several very important conceptions and results. These were extended in 1898 in a second paper dealing largely with development.<sup>1</sup> They considered that the ordinary exponential law<sup>2</sup> for the absorption of light in homogeneous media held for the photographic image and confirmed this view experimentally. They gave the following terminology, which has been generally accepted:—

$$\text{Transparency, } T = \frac{I}{I_0} = \frac{\text{intensity transmitted}}{\text{intensity incident}}$$

$$\text{Opacity, } O = \frac{I_0}{I} = \frac{1}{T}$$

$$\text{Density, } D = -\log_e T = \log_e O$$

D, the density, is for convenience usually taken as  $-\log_{10} T$ , and the experiments detailed in the foregoing chapter fully confirm Hurter and Driffield's view that D is proportional to the mass of silver per unit area.<sup>3</sup>

Reference to the work on exposure and development will be made in the course of the present work. Many of their conclusions have been controverted<sup>4</sup> chiefly from isolated experiments. Nevertheless, their method of sensitometry has been nominally adopted for commercial purposes in England. It has, however, been attacked by Dr. Eder<sup>5</sup> in the course of his important researches on sensitometry.

The authors have dealt elsewhere with the question of sensitometry, with the result of confirming in general the results of Hurter and Driffield.

<sup>1</sup> *Phot. Journ.*, 1898; *Eder's Jahrbuch*, 1899.

<sup>2</sup> Bunsen and Roscoe, *Pogg. Ann.*, 95-100.

<sup>3</sup> Cf. Eder, *Beiträge zur Photochemie u. Spectral-analyse*, 1904; Luther, *Zeit. f. Phys. Chem.*, 1900 (Ref.), recommends the term "Extinction," instead of the anomalous "density," as this quantity is the same as the "Extinction coefficient" introduced by Vierordt in absorption-photometry.

<sup>4</sup> For a bibliography of this controversy, see C. E. K. Mees and S. E. Sheppard, "Instruments for Sensitometry," *Phot. Journ.*, 44. No. 7, 222; and "On Sensitometry," *ibid.*, No. 9.

<sup>5</sup> *Loc. cit.*, *supra*, or *Sitzber. d. Wien. Akad.*, 1899, 113. sect. A.

Applications of physico-chemical doctrine to photographic phenomena may be found in the short-lived *Archiv f. wiss. Phot.*,<sup>1</sup> and, in especial, Abegg's "silver-germ" theory of exposure and development. This is dealt with later.

All developers are, chemically speaking, reducing agents, but the converse does not hold. In connection with this, Bredig<sup>2</sup> has pointed out the importance of the "reduction potential"<sup>3</sup> as a function of the developer. However, as there is no strict proportionality between "potential" and reaction velocity,<sup>4</sup> other conceptions are necessary, if the "efficiency" of developers is to be measured. The relation, as has been pointed out, may be conceived as analogous to Ohm's law,  $\text{velocity} = \frac{\text{potential}}{\text{resistance}}$ ,<sup>5</sup> and this "resistance" in chemical reactions is a term difficult to define or measure.

The chemistry of organic developing agents has been extensively investigated by Messrs. Lumière and Dr. Andresen,<sup>6</sup> to whom we owe the following rule:—All organic developers are substituted aromatic derivatives, containing two of the groups OH and NH<sub>2</sub>, joined by an ortho- or para-linking, the meta-bodies not acting as developers. Andresen<sup>7</sup> has pointed out the analogy between these bodies and the simple inorganic types, O<sub>2</sub>H<sub>2</sub>, hydrogen peroxide, N<sub>2</sub>H<sub>4</sub>, hydrazine, and NH<sub>2</sub>·OH, hydroxylamine, all of which function as developers. It seems possible that the quantitative investigation of development might throw light on the affinities of a large group of organic bodies.

Owing to the complications present in organic developing solutions, the reaction was first studied with ferrous salts, those employed being ferrous oxalate, citrate, and fluoride. These can be easily estimated analytically, and disturbing side

<sup>1</sup> *Archiv. f. Wiss. Phot.*, 1899–1900.

<sup>2</sup> *Eder's Jahrbuch*, 1895.

<sup>3</sup> Bancroft and Neumann, *Zeit. phys. Chem.*, **10**, 387; Nernst, *Theoret. Chem.*, 4te Auflage, 710.

<sup>4</sup> Ostwald, *Lehrbuch*, 2te Bd., 2te Tl. (2te Auflage).

<sup>5</sup> Nernst, *Theoret. Chem.*, 4te Auflage, 656.

<sup>6</sup> *Photo. Bulletin*, 1895, et seq.; *Eder's Jahrbuch*, 1899, 140–147.

<sup>7</sup> *Phot. Corr.*, 1899, 212; *Eder's Jahrbuch*, 1899, 140–147.

reactions do not occur to any extent. The methods and conclusions arrived at can then be applied to the study of other developing agents.

### METHOD OF INQUIRY AND SOURCES OF ERROR

The apparatus used was that described in Part I., Chap. II. Beside the accuracy of the light-source and of the photometric measurement, we have to consider—

**Errors due to Plates.**—Unevenness in the coating of the plates introduces a large source of errors. In these researches, Wratten ordinary emulsion specially coated on patent plate glass was used, the edges being rejected. Nevertheless, as the following figures show, the error from this source is considerable. Plates similarly exposed and developed, resulted as below:—

	(a)	(b)	(c)
1 . . . .	1'364	1'336	1'403
2 . . . .	1'329	1'342	1'354
3 . . . .	1'289	1'321	1'247
4 . . . .	1'287	1'349	1'280
5 . . . .	1'337	1'375	1'340
	<hr/>	<hr/>	<hr/>
Mean	1'3212	1'345	1'325
Greatest dev.	3'2 per cent.	2'2 per cent.	6'0 per cent.

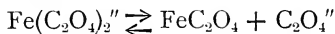
From these and other measurements it was calculated that from this cause alone the probable error on a single developed density is 1 per cent.<sup>1</sup> The authors have since constructed an instrument for the more exact coating of plates.

**Method of Development and Developer.**—The thermostat and plate-holders have already been described. Previous to development, the plates were soaked for 2 to 3 minutes in a tube of distilled water in the thermostat. Development was stopped by plunging the plates in cold water, they were washed, fixed in pure hypo, washed, cleared in dilute HCl,

<sup>1</sup> *Loc. cit.*, "Instruments for Sensitometry," *Phot. Journ.*, 1904, No. 7.

rinsed, wiped with cotton wool, and dried at a uniform temperature.

The developer first used was ferrous oxalate. A physico-chemical investigation had shown that the iron was present as a complex anion<sup>1</sup>  $\text{Fe}(\text{C}_2\text{O}_4)_2''$ , which is stable in the presence of excess of free oxalate ions, according to the equilibrium—



When the ferrous oxalate is present in solid form, the constant for the above equilibrium is 0.37 at 20° C. The standard solutions employed were—

A.  $\text{FeSO}_4$ , 278 grammes per litre, molecular

B.  $\text{K}_2\text{C}_2\text{O}_4$ , 184        "        "        "

checked by titration with standard  $\text{KMnO}_4$ .

The developer was always slightly acidified with pure  $\text{H}_2\text{SO}_4$ .

**The Velocity of Development.**—This was studied by measuring the growth of the density, *i.e.* the mass of silver, with the time of reaction, in full analogy with other kinetic investigations. The following facts were experimentally proved :—

(a) The silver deposited increases rapidly at first, then more slowly, and finally tends to a limit.

(b) This limit depends only on the exposure.<sup>2</sup>

(c) The velocity depends upon the concentration of the reducer.

(d) A soluble bromide reduces the velocity, but the "slowing off" with time is not so pronounced.

Temperature was always 20.0° C., unless otherwise stated.

Table I for *a*, *b*, and *c*.

Developer A,	5 c.c.	$\text{FeSO}_4$ ,	M/1.	Exposure 10 C.M.S.
	45	"	$\text{K}_2\text{C}_2\text{O}_4$ ,	M/1.
"	B,	2	"	$\text{FeSO}_4$ ,
			M/1.	Exposure 50 C.M.S.
	48	"	$\text{K}_2\text{C}_2\text{O}_4$ ,	M/1.

<sup>1</sup> *Proc. of Chem. Soc.*, **21**, No. 288, 10.

<sup>2</sup> Apparent exceptions to this law will be discussed in subsequent work.

TABLE I.

A. Time.	Density.	B. Time.	Density.
5'0 mins.	1'052	5'0 mins.	0'628
10'0 "	1'230	10'0 "	0'987
20'0 "	1'296	15'0 "	1'323
45'0 "	1'444	20'0 "	1'376
90'0 "	1'591	30'0 "	1'528
120'0 "	1'623	90'0 "	2'429

and confirming *a*, *b*, *d*.

Developer, 4'0 c.c.  $\text{FeSO}_4$ , M/1.

40'0 "  $\text{K}_2\text{C}_2\text{O}_4$ , M/1.

1'0 "  $\text{KBr}$ , N/10.

to 50'0 " with  $\text{H}_2\text{O}$ .

TABLE 2.

$D_9 = 50$  C.M.S.

$D_9 = 50$  C.M.S.

Time.	Density.	Time.	Density.
5'0 mins.	0'256	10'0 mins.	0'522
11'0 "	0'759	15'0 "	0'741
15'0 "	1'001	20'0 "	0'838
20'5 "	1'375	30'0 "	0'939
25'0 "	1'435	40'0 "	1'050
31'0 "	1'541	50'0 "	1'185
40'0 "	1'847	60'0 "	1'212
50'0 "	2'119	75'0 "	1'360
60'0 "	2'148	90'0 "	1'409
70'0 "	2'333	105'0 "	1'574
90'0 "	2'398	135'0 "	1'641
120'0 "	2'398	12 hours	1'641

These facts are in agreement with Hurter and Driffeld's statement that development tends to a limit depending upon the exposure. They considered that their results were represented by the formula  $D = D_x(1 - a^t)$ ,<sup>1</sup> where  $D$  = density at time  $t$ ,  $D_x$  = ultimate density, and  $a$  is a constant. They

<sup>1</sup> *Journ. Soc. of Chem. Ind.*, May, 1890.

stated that this was arrived at "on the idea that the number of silver bromide particles affected by light is greatest in the front layer of the film, and decreases in geometrical progression as each successive layer is reached," and "that the developer reduced the particles as it penetrated the film." Apart from the inherent improbability of this process taking place so regularly, it would, as was pointed out by Luggin,<sup>1</sup> give results in contradiction to the law of constant-density ratios demonstrated later. A conclusive experimental disproof of the hypothesis is given by the fact that a plate exposed from the glass side develops normally, although in this case the layer containing fewest reduced particles is reached by the developer first.

TABLE 3.

Time.	Density.	K.
11'0 mins.	0'477	0'0210
15'0 "	0'612	0'0217
20'0 "	0'681	0'0193
33'0 "	0'897	0'0197
75'0 "	1'156	For meaning of K, see later.
120'0 "	1'156	

The mass-time curve is quite normal.

Another theory of development-velocity was proposed by Dr. Abegg,<sup>2</sup> based on his "silver-germ" theory of the latent image. According to this, the velocity of development, *i.e.* the number of silver germs deposited in unit time, is proportional to the number present at any time. This may be expressed by  $v = dx/dt = k(a + b + x)$ , where  $a$  and  $b$  are constant numbers of germs due to exposure and ripening respectively, and  $x$  is the number due to development. It is evident that as  $x$  increases the velocity should increase, and a steady acceleration should be noticed till the whole film was developed

<sup>1</sup> *Zeit. phys. Chem.*, **23**, 622.

<sup>2</sup> R. Abegg, *Archiv f. wiss. Phot.*, 1899, 1.

through; in this unmodified form the expression is in obvious disagreement with the facts of development.

**Theory of Development.**—The investigations of Boguski,<sup>1</sup> Noyes and Whitney,<sup>2</sup> and especially of M. Wilderman,<sup>3</sup> E. Bruner, and Nernst,<sup>4</sup> have led to a better understanding of the reaction-velocity in heterogeneous systems, among which the development of silver-bromide naturally stands. When a solid dissolves, the rate is proportional to its surface and to the difference between the saturation-concentration and that at the given moment. At the boundary between the phases saturation exists, so that the rate of solution depends on the diffusion velocity. When a chemical action is superposed, Nernst assumes that in most cases the equilibrium in the reaction-layer is adjusted with practically infinite velocity compared with the diffusion process. If the length of the diffusion path and the diffusion coefficients are known, in many cases the velocity may be calculated in absolute measure.

Now, the chemical equation for development with ferrous oxalate is probably  $\text{Ag} + \text{Fe}(\text{C}_2\text{O}_4)_2'' = \text{Ag} + \text{Fe}(\text{C}_2\text{O}_4)_2'$ , *i.e.*  
(met.)  
 one silver ion is converted into metallic silver. The velocity equation will then be  $dx/dt = K C_{\text{Ag}} \cdot C_{\text{FeOx}}''$ .

$C_{\text{Ag}}$  may be reckoned as constant on the above view of the instantaneous adjustment of the equilibrium, as solid AgBr is present. If we assume a layer of constant thickness,  $\delta$ , in which diffusion takes place, then there will diffuse into the reaction-layer  $S \frac{\Delta}{\delta} (a - x) dt$  of reducer in the time  $dt$ , where  $\Delta$  is the diffusion coefficient of the reducer,  $a$  its initial concentration, and  $x$  the equivalents of AgBr reduced. If  $x$  be very small compared with  $a$ , the total concentration, this becomes  $S \frac{\Delta}{\delta} a \cdot dt$ , and the velocity of development is given by

<sup>1</sup> *Vide Ostwald, Lehrbuch, 2te Auflage, 2te Bd., 2te Fl., Chem. Kinetik.*

<sup>2</sup> *Zeit. phys. Chem.*, **23**.

<sup>3</sup> M. Wilderman, *Phil. Mag.*, October, 1902; *Zeit. phys. Chem.*, 1899, **30**, 341.

<sup>4</sup> *Zeit. phys. Chem.*, 1904, **47**, 56.

$dx/dt = KS$ , where  $S$  is the surface of the solid phase, and  $K = \Delta \cdot a/\beta$ . Now the existence of a maximum and fixed quantity of developable  $\text{AgBr}$  is proven by the experiments detailed above. We shall distinguish the amount of this by  $(\text{AgBr}')$ , and in the course of the reaction it varies from  $(\text{AgBr}')$  to  $O$ . The surface  $S$ , therefore, also varies from  $\phi(\text{AgBr}')$  to  $O$ . Now, the microscopic examination of the photo-film shows that it consists of a number of very fine  $\text{AgBr}$  grains embedded in gelatine. This, and the fact that the emulsion absorbs light, according to the law  $I/I_0 = e^{-m}$ ,<sup>1</sup> where  $m$  is the mass of haloid, allow us to substitute for  $S = \phi(\text{AgBr}')$ ,  $S = p(\text{AgBr}')$ , *i.e.* the surface is directly proportional to the mass of  $\text{AgBr}'$  at any time, and therefore to its optical density. The optical density  $D_0$  of the latent image  $(\text{AgBr}')$  must equal  $D_\infty$ , the density reached on ultimate development, while, obviously, the density of the  $(\text{AgBr}')$  at any time,  $t$ , equals  $D_\infty - D$ , where  $D$  is the density of reduced silver at the time  $t$ . Hence  $dD/dt = KS = K(D_\infty - D)$ , which gives on integration—

$$\frac{1}{t} \log \frac{D_\infty}{D_\infty - D} = K$$

If this formula be written  $D = D_\infty(1 - e^{-Kt})$ , it will be seen to be the same as Hurter and Driffeld's, when  $e^{-K} = a$ , but it has been obtained on quite general grounds, free from hypothesis, as to the nature or distribution of the developable haloid.

Tested experimentally, the first series gave a decreasing value for  $K$ . It was found that this was due to the accumulation of bromide, which lowered the velocity. This was avoided by adding excess of free bromide in such quantity that the amount due to development was negligible.

The following series give some of the results:—

<sup>1</sup> A fine-grained heterogeneity may be treated formally as a solution; cf. Bredig, "Anorganische Fermente," Leipzig, and Bodenstein, *Zeit. phys. Chem.*, 1904, **49**, 42.



TABLE 4.

$$K = \frac{1}{t} \log_{10} \frac{D_x}{D_x - D}$$

*Series I.**Series II.*

Time.	Density.	K.	Time.	Density.	K.
5'0 mins.	0'294	0'0144	5'0 mins.	0'370	0'0182
10'0 "	0'742	0'0212	10'0 "	0'683	0'0186
15'0 "	0'973	0'0205	15'0 "	0'999	0'0206
20'0 "	1'178	0'0207	20'0 "	1'203	0'0206
25'0 "	1'276	0'0190	25'0 "	1'270	0'0181
30'0 "	1'448	0'0203	30'0 "	1'479	0'0203
40'0 "	1'547	0'0180	160'0 "	1'962	
95'0 "	1'828	0'0195	∞	1'962	
135'0 "	1'899	0'0199			
∞	1'919				
Mean . . K = 0'01995			Mean . . K = 0'0194		

*Series III.**Series IV.*

Time.	Density.	K.	Time.	Density.	K.
5'0 mins.	0'311	0'0149	5'0 mins.	0'283	0'0190
10'0 "	0'838	0'0229	10'0 "	0'547	0'0208
15'0 "	1'000	0'0193	15'0 "	0'759	0'0217
20'0 "	1'266	0'0208	20'5 "	0'919	0'0214
25'0 "	1'401	0'0199	25'0 "	0'990	0'0203
∞	2'053		30'0 "	1'114	0'0217
			45'5 "	1'276	0'0209
			∞	1'437	
Mean . . K = 0'01992			Mean . . K = 0'0208		

Total mean of four series . . K = 0'0203

The developer was—

4'00 c.c.  $\text{FeSO}_4$  mol. }  $\text{Fe} = \text{N}/25$ .  
 2'00 "  $\text{KBr}$ ,  $\text{N}/10$  }  $\text{Br} = \text{N}/500$ .  
 40'00 "  $\text{K}_2\text{C}_2\text{O}_4$  mol.

To 100'0 c.c. with  $\text{H}_2\text{O}$ .

Another batch of the same emulsion gave—

Series I.  $K = 0.0191$ .      Series III.  $0.0217$ .

„ II.  $K = 0.0201$ .      Series IV.  $0.0204$ .

Total mean . . . . .  $0.0204$ .

Total mean of four series .  $K = 0.0203$ .

The following table and curve show that the expression is satisfactory over a wide range of development, considering the experimental difficulties. All the series,  $D_1$ ,  $D_2$ , and  $D_3$ , were reduced by common proportion to the same value:—

TABLE 5.  
Curve for N/500 Br. and N/25 Ferrous Oxalate.

Time.	$D_1$ .	$D_2$ .	$D_3$ .	D obs.	D calc.
5'0 $\frac{1}{2}$ mins.	0.330	0.303	0.373	0.335	0.410
10'0 „	0.773	0.815	0.697	0.762	0.736
15'0 „	1.013	0.975	1.020	1.003	0.995
20'0 „	1.227	1.232	1.228	1.229	1.201
25'0 „	1.330	1.365	1.296	1.330	1.364
30'0 „	1.510		1.510	1.510	1.495
40'0 „	1.610			1.610	1.681
95'0 „	1.904			1.904	1.960
135'0 „	1.970			1.970	1.980
$\infty$	2.000	2.000		2.000	2.000

It appears that generally the value of  $K$  is constant for a standard emulsion freshly coated. Variations, however, may be caused by different emulsification, and the value varies with different plates. Thus—

Wratten ordinary,  $K = 0.0203$

Barnet ordinary,  $K = 0.0260(0.0249 - 0.0254)$

For occasions of space the mean value of  $K$  with the extremes are given, except where it seems desirable to show that the course of the reaction is unchanged.

**Influence of Concentration on the Velocity.**—The constant as developed above contains implicitly  $C_{Fe}$ , the total concentration of the iron; it should, therefore, be proportional to this experimentally.

TABLE 6.

C ferrous oxalate.	K found.	
N/12.5	0.4011	Br = N/500
N/12.5	0.4061	
N/25	0.203	
N/50	0.100	
N/50	0.102	

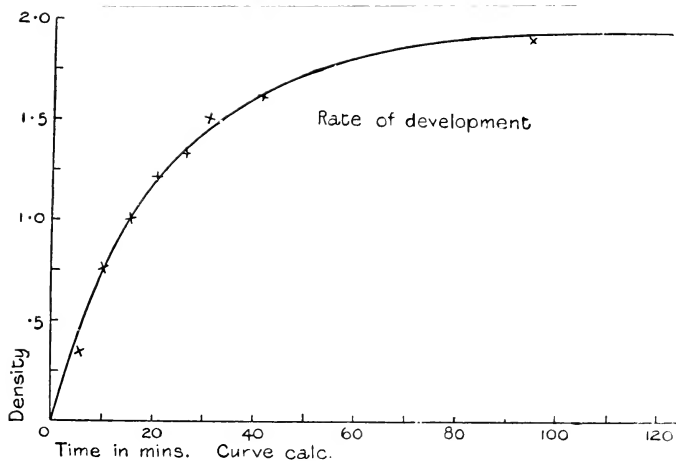


FIG. 14.

The values for N/12.5 showed some tendency to decrease; this is probably due to the rapid accumulation of bromide and other reaction products, which do not diffuse rapidly, and so influence the velocity by remaining in the reaction layer, a fact which is one of the main causes of divergencies and difficulties in heterogeneous reactions.<sup>1</sup> A more stringent proof of the proportionality is given later.

On the diffusion theory of the development velocity, this proportionality is simply the expression of the fact that the amount of reducer diffusing into the reaction layer is proportional to the concentration (*vide* p. 51). Nernst<sup>2</sup> has pointed out that on this theory it is not admissible to draw

<sup>1</sup> Ostwald, *Lehrbuch*, 2te Auflage, 2te Bd., *Chem. Kinetik*.

<sup>2</sup> W. Nernst, *Theoretische Chemie*, 4te Auflage, 573.

conclusions as to the order of the reaction in heterogeneous systems, so that the otherwise probable theory, that the reaction is mono-molecular with respect to iron, cannot be regarded as strictly proven by this.

**The Influence of Bromide on the Velocity.**—The “restraining” influence of soluble bromides is well known to photographers. Preliminary measurements indicated a rather complicated induction; the question is dealt with very fully in Chap. III., Part II., where the question of equilibrium is considered, and a more complete theory of the mechanism of development propounded.

**Age of Plate.**—In the course of this work, it was found that the velocity of development depends largely on the age of the plate, diminishing with keeping. This change is accelerated by heat and atmospheric conditions. This was discovered when plates of Batch I were used a considerable time after making, and gave quite divergent velocities according as they had been kept. The phenomenon, while the cause was still unsuspected, caused much trouble. The following tables exhibit the divergencies obtained:—

TABLE 7.  
Developer Fe = N/25, KBr = N/500, K = 0.0203.<sup>1</sup>

Time.	Density.	$K = \frac{1}{t} \log \frac{D_x}{D_x - D}$
15.0 mins.	0.259	0.0048
20.0 „	0.452	0.0066
30.0 „	0.643	0.0068
40.0 „	0.816	0.0070
50.0 „	0.960	0.0071
60.0 „	1.042	0.0068
70.0 „	1.089	0.0062
80.0 „	1.214	0.0067
90.0 „	1.302	0.0069
100.0 „	1.333	0.0065
120.0 „	1.423	0.0064
12 hrs	1.713	
14 „	1.712	

Mean, K = 0.0067, *i.e.* a reduction to one-third of its former value. This was for an opened box kept in laboratory cupboard.

<sup>1</sup> See Table 4, p. 53.

TABLE 8.

Developer Fe = N/25, Br' = N/500.

Time.	Density.	K.
10'0 mins.	0'226	0'0062
15'0 "	0'575	0'0118
25'0 "	0'713	0'0094
30'0 "	0'835	0'0097
40'0 "	1'041	0'0102
50'0 "	1'185	0'0102
60'0 "	1'284	0'0101
70'0 "	1'411	0'0108
80'0 "	1'432	0'0099
190'0 "	1'666	
6 hrs.	1'708	
K = 0'01004		

TABLE 8a.

Fe = N/25, Br' = N/1000.

Time.	Density.	K.
10'0 mins.	0'552	0'0174
16'5 "	0'744	0'0185
20'0 "	0'891	0'0166
25'0 "	0'900	0'0136
30'0 "	1'040	0'0141
40'0 "	1'277	0'0157
50'0 "	1'375	0'0151
60'0 "	1'403	0'0134
175'0 "	1'646	
∞	1'669	
K = 0'01555		

The values obtained six months before were—

N/500 Br', K = 0'0203.

N/1000, K = 0'0280,

so that in this case the speed has been about halved. This was for a sealed box kept in laboratory cupboard.

Further, for an opened box kept in college locker—

TABLE 9.

N/500 KBr, K = 0'0203.

Time.	Density.	K.
10'0 mins.	0'513	0'0156
15'0 "	0'809	0'0195
20'0 "	1'002	0'0200
26'0 "	1'115	0'0185
30'0 "	1'174	0'0180
45'0 "	1'418	0'0184
60'0 "	1'560	0'0190
190'0 "	1'664	
3 hrs.	1'664	
Mean . . K' = 0'0189.		

TABLE 9a.

N/200 KBr, K = 0'0170.

Time.	Density.	K.
10'0 mins.	0'549	0'0149
15'0 "	0'835	0'0168
20'0 "	0'961	0'0163
25'0 "	1'119	0'0155
30'0 "	1'274	0'0161
40'0 "	1'461	0'0160
46'0 "	1'562	0'0164
60'0 "	1'688	0'0162
∞	1'895	
Mean . . K' = 0'01603.		

In this case a reduction of only 5 per cent. in the velocity has taken place.

These measurements show that the rate at which a plate develops is diminished with time of keeping. Apparently a slow irreversible change takes place in the film, which is accelerated by heat and presence of gases, etc. If we consider the expression for the velocity  $K = \Delta/\delta \cdot \alpha$ , it seems probable that the alteration is due to an effect on  $\Delta$ , the diffusivity coefficient. It is quite different from that produced by so-called "hardening" agents, which do not affect the development velocity.

Only the absolute value of the velocity, and not the velocity-function, is altered.

**The Diffusion Path,  $\delta$ .**—In his work on heterogeneous reactions, Brunner measured the thickness of the diffusion layer by electro-chemical reactions, and found, for example, for rate of solution in water of benzoic acid, 0.03 mm. In general, the layer was of this order, but was lessened as the rate of stirring increased.

In the photo-film the diffusion path must be equal to the depth of the latent image plus a small layer on the gelatine surface. The former is not alterable by stirring, and the subsequent microscopic measurements show that it is of about the same order as Brunner found, viz. about 0.02 to 0.03 mm. The outer layer is alterable by rotation, but is probably not very large, as increasing the rotation had but a slight effect on the velocity. Unfortunately, very high velocities of stirring increased the fog materially, and also produced uneven marking. A rate of about 30 revolutions per minute was found to ensure homogeneity of the solution on the bounding surface.

It should be noticed that the whole mass and surface of the developable image in the case of development lie in the short diffusion layer in the gelatine. How far this modifies the Nernst theory for the reaction-velocity will be considered later.

A slight periodicity in the rate of development was sometimes noted : see curve.<sup>1</sup>

<sup>1</sup> Cf. Ostwald, *Vorles. über Naturphil.*, Leipzig, 1902, 274, 315, 362 ;

**Note on Fog.**—It is usual in density measurements to subtract the so-called “fog” from the total density. This is the density due to inherent fog in the plate, extraneous light, etc. Usually a separate reading is made of the so-called fog strip, but, owing to the differential nature of our instrument,

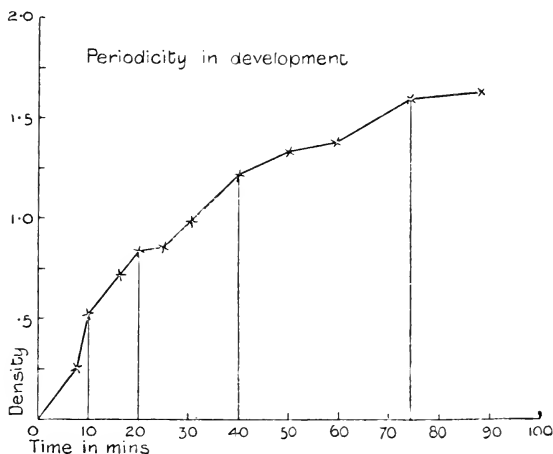


FIG. 15.

the “fog” reading was automatically subtracted, and taken from the same portion of emulsion as the exposure.

But the formula  $\frac{1}{t} \log \frac{D_x}{D_x - D} = K$  shows that there is a theoretical error in assuming the fog in the unexposed strip is equal to that in the exposed strip.

For let  $A + B = C$  be total mass AgBr, where  $A = \text{AgBr}$  changed by light,  $B = \text{AgBr}$  unchanged.

Then rate of fogging  $= (dD/dt)C = K(A + B)$  in fog strip, and equals  $(dD/dt)B = KB$  in exposed film.

Obviously, fog increases faster in unexposed film than in the exposed; it is desirable, therefore, for photo-chemical investigations, to have an emulsion which does not give fog-

density higher than 0·15 to 0·2, even on infinite development, and in most of this work this was fulfilled.

**Law of Constant-Density Ratios.**—Another deduction from the development formula is the law of constant-density ratios. If a series of increasing exposures are given to a plate, as every density increases proportionately, the ratio of the densities due to any two exposures is constant, and independent of the time of development.

Hurter and Driffield showed that if a geometrically increasing series of exposures be given to a plate over a certain range, the density increased arithmetically. Over this period of "correct exposure" the following equation holds:  $D = \gamma \log E/i$ , where  $E$  is the exposure,  $i$  is a characteristic constant of the plate, termed the inertia, and  $\gamma$  is a constant depending upon the development, and called the development factor. The magnitudes  $i$  and  $\gamma$  are obtained graphically as follows: the densities due to nine successive exposures are plotted as ordinates, and the logarithms of the corresponding exposures as abscissæ. A curve is obtained which, for a certain period, is practically a straight line. The point where this cuts the exposure axis gives  $\log i$ , and if  $\theta$  be the angle of inclination,  $\gamma = \tan \theta$ . Analytically, the value of  $\gamma$  may be deduced as follows: for two exposures,  $E_1$  and  $E_2$ , we obtain the densities  $D_1$  and  $D_2$ , the equations being—

$$D_1 = \gamma \log E_1/i \quad D_2 = \gamma \log E_2/i$$

Eliminating  $i$ —

$$\gamma = \frac{D_2 - D_1}{\log E_2 - \log E_1} = \frac{\Delta D}{\Delta \log E}^1$$

$\gamma$  is therefore independent of the absolute exposure, and only dependent on the  $E_2/E_1$  which is fixed by the sector-wheel.<sup>2</sup>

In order to test the constancy of the density ratios, two plates were exposed simultaneously in the sensitometer to avoid

<sup>1</sup> Or  $D = \gamma \frac{\log E}{i}$ , hence  $\gamma = \frac{dD}{d \log E}$ .

<sup>2</sup> For calibration of sector-wheel, *vide* p. 18.



errors due to light inconstancy, and developed for different times. The values of  $\gamma$  were obtained from the curves in the graphic manner described. Each plate was allowed 100 c.c. of developer.

$\text{FeSO}_4$  mol. 8.0 c.c. +  $\text{K}_2\text{C}_2\text{O}_4$  mol. to 100 c.c.

The logarithms of the exposures are given on an arbitrary scale, putting  $\log E_9 = 1.0$ , as the absolute value is unimportant. A typical table is given below—

TABLE 10.

$T_1 = 2$  mins.,  $T_2 = 6$  mins.

No.	Log E.	Density $T_1$ .	Density $T_2$ .	Ratio $D_1/D_2$ .
1	3.30	—	—	—
2	3.012	0.876	2.563	2.935
3	2.72	0.759	2.230	2.900
4	2.42	0.685	1.995	2.920
5	2.14	0.499	1.491	2.983
6	1.80	0.332	1.096	3.330
7	1.575	0.234	0.716	3.050
8	1.360	0.128	0.329	2.680
Mean . .				2.957

Other results abbreviated—

Series II.	$R = 1.465$ .	Mean dev. = $\mp 0.04$ .	$T_1 = 6$ mins.
			$T_2 = 120$ „
„ III.	$R = 2.21$ .	„ = $\mp 0.04$ .	$T_1 = 2$ „
			$T_2 = 4$ „
„ IV.	$R = 1.49$ .	„ = $\mp 0.05$ .	$T_1 = 8$ „
			$T_2 = 120$ „
„ V.	$R = 1.353$ .	„ = $\mp 0.032$ .	$T_1 = 5$ „
			$T_2 = 10$ „
„ VI.	$R = 1.48$ .	„ = $\mp 0.05$ .	$T_1 = 10$ „
			$T_2 = 120$ „

Range of exposure, 1 to 250.

„ development, 2 mins. to 2 hrs.

The ratios of densities due to different exposures are unchanged by time of development in a non-bromided developer.

These tables and the curves show that for variations in the time of development from 2 minutes the density ratios and the values of  $i$  are unaffected. Every density grows proportionately with the time, a fact which finds its rational explanation in the theory of development proposed.

For the straight-line portion of exposure the equation  $D = \gamma(\log E - \log i)$  holds, and for a single density the

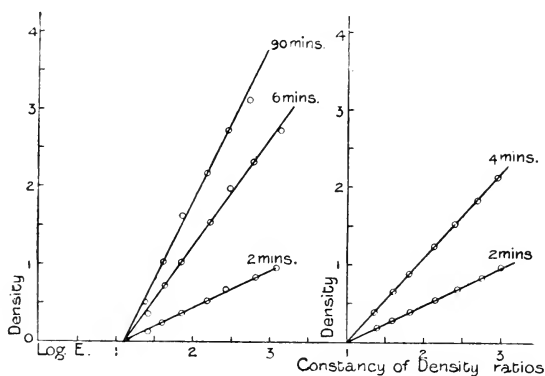


FIG. 16.

expression in brackets is a constant. The development factor,  $\gamma$ , is therefore strictly proportional to  $D$ , and as—

$$D = D_x (1 - e^{-Kt})$$

$$\text{so } \gamma = \gamma_x (1 - e^{-Kt})$$

where  $\gamma = \gamma$  at time  $t$ ,  $\gamma_x = \gamma$  infinite dev., which gives the relation between  $\gamma$  and the time of development.

The following tables show the validity of the expression for different batches of plates :—

TABLE 11.

Time.	Development factor $\gamma$ .	$\frac{1}{t} \log_{10} \frac{\gamma_x}{\gamma_x - \gamma}$ .
2'0 mins.	0'50	0'0460
2'5 "	0'73	0'0562
4'0 "	1'08	0'0572
5'0 "	1'33	0'0608
6'0 "	1'47	0'0578
8'0 "	1'77	0'0602
10'0 "	1'91	0'0541
15'0 "	2'17	0'0480
$\infty$	2'67	
Mean . .		0'0550

TABLE 12.

Time.	$\gamma$ .	$K = \frac{1}{t} \log \frac{\gamma_x}{\gamma_x - \gamma}$ .
2'0 mins.	0'684	0'0495
2'5 "	0'840	0'0500
4'0 "	1'23	0'0500
5'0 "	1'63	0'0470
8'0 "	1'90	0'0470
$\infty$	3'40	
Mean . .		$K = 0'0487$

This shows that both  $\gamma_x$  and  $K$  vary for different batches; for the same developer,  $\gamma_x$  and  $K$  are the characteristic development constants of the emulsion.

The factor  $\gamma$  is of considerable importance in practical photography, as it measures the gradation or degree of contrast in a negative.

**Influence of Concentration on  $\gamma$ .**—As might be expected, this is simply the time taken to reach a given factor is inversely as the concentration of the ferrous oxalate.

Thus for N/12.5 and N/25 ferrous oxalate—

N/25	. . .	5.0 mins.	. . .	$\gamma = 0.73$
N/12.5	. . .	2.5 „	. . .	$\gamma = 0.72$
N/25	. . .	5.0 „	. . .	$\gamma = 1.54$
N/12.5	. . .	10.0 „	. . .	$\gamma = 1.59$

Over the range N/5 to N/40—

(A) N/5	. . .	1.5 mins.	(C) N/20	. . .	6.0 mins.
(B) N/10	. . .	3.0 „	(D) N/40	. . .	12.0 „

TABLE 13.

E.	Log E.	D <sub>A</sub> .	D <sub>B</sub> .	C <sub>C</sub> .	D <sub>D</sub> .	Mean D.
304.5	2.48	—	1.358	1.440	1.446	1.414
154.8	2.19	1.302	1.248	1.278	1.270	1.274
78.0	1.89	1.094	1.114	1.104	1.120	1.108
40.6	1.61	0.892	0.892	0.902	0.850	0.884
18.8	1.26	0.604	0.688	0.676	0.608	0.644
11.1	1.05	0.422	0.436	0.428	0.358	0.414
6.72	0.83	—	0.244	—	—	0.244

*The velocity of development is proportional to the concentration of the ferrous oxalate.*

The magnitude  $\gamma_x$ , i.e. the limiting  $\gamma$  of the plate, is of great importance. It expresses numerically the ultimate density-giving powers of plates, and gives a numerical measure of the quality that has hitherto been expressed by such phrases as “contrasty plates,” soft plates, “flaue platten,” and so forth.  $\gamma_x$  is proportional to the photometric constant of the reduced silver, and so varies slightly with the developer, but more so with the emulsification of the haloid.

The practical estimation of  $\gamma_x$  and  $D_x$  is in many cases beset with much experimental difficulty. If  $\gamma_x$  is very high, the resultant densities are hard to measure, while many commercial plates, especially rapid ones, give much fog on prolonged development. Since the equilibrium is only theoretically reached after infinite time, only a close approximation is reached by very long development. The method given by

Ostwald<sup>1</sup> for evaluating the end-result was employed to check the results.

The following method of obtaining  $\gamma_x$  and K from simultaneous values of  $\gamma$  and  $t$  was pointed out by Dr. L. N. G. Filon :—

Writing the equation  $\frac{1}{t} \log_e \frac{\gamma_x}{\gamma_x - \gamma} = K$  in the form  $\gamma = \gamma_x(1 - e^{-Kt})$ , and taking  $\gamma_1$  and  $\gamma_2$ , so that  $t_2 = 2t_1$ , we get—

$$\gamma_1 = \gamma_x(1 - e^{-Kt_1}) \quad . \quad . \quad . \quad . \quad (a)$$

$$\gamma_2 = \gamma_x(1 - e^{-Kt_2}) \quad . \quad . \quad . \quad . \quad (b)$$

putting  $e^{-Kt_1} = x$ , we have from (a) and (b) —

$$\frac{\gamma_1}{\gamma_2} = \frac{1 - x}{(1 - x^2)} = \frac{1}{1 + x} = \frac{1}{1 + e^{-Kt_1}}$$

$$\therefore \frac{\gamma_2 - \gamma_1}{\gamma_1} = e^{-Kt_1} \quad \frac{\gamma_1}{\gamma_2 - \gamma_1} = e^{Kt_1}$$

$$\text{and} \quad \frac{1}{t} \log_e \frac{\gamma_1}{\gamma_2 - \gamma_1} = K$$

which gives K, whence  $\gamma_x$  may be obtained by substitution ; but it must be noticed that the expression only holds when  $\gamma_2/\gamma_1 = < 0.8$  approximately, *i.e.* when the tangential part of the curve is past.

**Comparison of Developers.**—By means of the  $\gamma$  formulæ the relative efficiencies for different developers can be compared. The following results give the comparison for ferrous oxalate, fluoride, and citrate :—

**Ferrous Fluoride.**—The use of this salt was suggested by Peters' work on the reduction potential of ferrous salts. Luther explains the fact that ordinary ferrous salts— $\text{Fe}''\text{R}$ —as  $\text{FeSO}_4$  do not develop as due to the reversal of the reaction by ferric ions. But Peters has shown that the E.M.F. of a ferrous chain is very much increased by the addition of a soluble fluoride, owing to the fact that  $\text{Fe}'''\text{Fl}_3$  is but slightly dissociated, and further, that a complex ferrid-fluoridion is formed, both causes tending to remove ferric ions. We found that an N/10 solution of  $\text{FeSO}_4$  in excess of KF developed but slowly.

<sup>1</sup> *Lehrbuch*, 2te Auflage, 2 Th., 2 Bd., 210.

Prolonged development removed the film from the plate, so that celluloid films had to be used.

The developer was made by mixing  $\text{FeSO}_4$  and  $\text{NaF}$  solutions, as the sodium double salt seems more soluble than the potassium one. The solutions were nearly colourless.

TABLE 14.

Ferrous oxalate, N/10.		
Time.	$\gamma$ .	$\frac{1}{t} \log_{10} \frac{\gamma_{\infty}}{\gamma_{\infty} - \gamma}$
Temp. 13° C.		
3·0 mins.	0·64	0·056
6·0 "	1·13	0·060
8·0 "	1·39	0·064
$\infty$	2·00	—
		K = 0·060
Temp. 20° C.		
2·0 "	0·49	0·062
4·0 "	1·01	0·076
7·0 "	1·35	0·071
8·0 "	1·49	0·074
$\infty$	2·00	—
		K = 0·071

$\gamma_{\infty} = 2·00$ , mean value found by Filon's expression.

The experiments with ferrous fluoride showed that the law of the constancy of inertia with time of development held here. For brevity, only the  $\gamma$  values are given.

TABLE 15.

Ferrous fluoride, N/10.

Time.	$\gamma$ .	$\frac{1}{t} \log_{10} \frac{\gamma_x}{\gamma_x - \gamma}$
	Temp. 13° C.	
45'0 mins.	0'50	0'0028
90'0 „	1'00	0'0033
135'0 „	1'35	0'0036
280'0 „	1'72	0'00303
$\infty$	2'00	
		K = 0'0032
	Temp. 20° C.	
15'0 „	0'204	0'0030
60'0 „	0'895	0'0043
90'0 „	1'22	0'0045
120'0 „	1'36	0'0041
$\infty$	2'00	
		K = 0'0043

Hence, comparing results—

Temp.	K, Ferrous oxalate.	Ferrous fluoride.	Ratio.
13° C.	0'060	0'0032	18'7
20° C.	0'071	0'0043	16'5

This indicates that ferrous fluoride has a somewhat higher temperature-coefficient than ferrous oxalate.

*Ferrous Citrate.*—This is a good developer for chloride plates, but develops silver bromide very slowly. For the plates employed  $\gamma_x = 3'40$ , and K for ferrous oxalate at 20° C. = 0'0487.

It was found that here also the density ratios and the inertia were independent of the time of development. For the velocity at 20° C.—

TABLE 16.

Ferrous citrate, N/10.

Time.	$\gamma$ .	$\frac{1}{t} \log_{10} \frac{\gamma_{\infty}}{\gamma_{\infty} - \gamma}$
60.0 mins.	0.474	0.0011
120.0 „	0.720	0.0009
240.0 „	1.40	0.00096
$\infty$	3.40	<hr/> K = 0.0010

Whence for table of relative efficiencies at 20° C.—

Developer.	Efficiency = K.
Ferrous citrate . . .	1.00
Ferrous fluoride . . .	2.95
Ferrous oxalate . . .	48.7

**On the Theory of Development.**—In the ferrous fluoride developer the reducing agent seems most probably the ferrous ion, the concentration of which is very high; with ferrous citrate a complex ferro-citratianion. Now, on the diffusion theory the great difference in the observed velocity is difficult to explain; in particular, the mobile ferrous ion should prove the most efficient reducer. It is possible that the electric relations between colloids and electrolytes would account for a diffusion resistance to the positive ferrous ion, or even that under these conditions the complex ferro-fluoranium, existing at a low concentration, forms the actual reducer. A further examination was made as to the physical nature of the film and of development, so that some idea as to the nature of the movement of the active substances in the film could be arrived at. Measurements were also made of the influence of temperature, since Bodenstein<sup>1</sup> has indicated its value as a criterion in heterogeneous reactions.

<sup>1</sup> M. Bodenstein, *Zeit. phys. Chem.*, 1904, **49**, 42.



## CHAPTER II

### THE MICROSCOPIC STUDY OF THE PHOTOGRAPHIC IMAGE

THE fact that both the silver halide and the resulting silver are distributed through the film in the form of particles of minute but measurable size permits a closer investigation of the photographic process by means of the microscope. Finer qualitative differences may be detected and independent conclusions drawn, while, moreover, the research can be pushed considerably below the normal limits in exposure and development. The size of the grain is of great importance both from a practical and from a theoretical point of view. For in the one case it imposes a limit on resolution for spectroscopic and astronomical photography, while, so far as theory is concerned, in heterogeneous processes the degree of surface extension of a condensed phase may be of the utmost moment.<sup>1</sup>

The method has been used previously by Abegg, Abney, Kaiserling, Ebert, and others,<sup>2</sup> but the most systematic and important inquiry is that of K. Schaum and V. Bellach.<sup>3</sup> The following investigation had been carried out in large part

<sup>1</sup> Ostwald, *Lehrbuch*, V. 3; Chem. Kinetik. Bredig, *Arch. f. wiss. Phot.*, 1900, *Eder's Jahrbuch*, 1899, p. 357. For spectro-photographic importance, see Kayser, *Hd.buch d. Spectroscopie*, II. 1905. E. C. C. Baly, *Spectroscopy*, 1905 (Longmans).

<sup>2</sup> H. Ebert, *Eder's Jahrbuch*, 1894, p. 14; Kaiserling, *Phot. Mit.*, 1898, I. and II.; Abney, *Phot. Journ.*, 1898; R. Abegg, *Arch. f. wiss. Phot.*, 1899, I. 109.

<sup>3</sup> K. Schaum and V. Bellach, *Physik. Zeit.*, 1901-2; and *Die Struktur d. Phot. Negative*, by V. Bellach (W. Knapp, Halle), 1903. This admirable monograph contains an extensive bibliography on many points in photographic processes.

before the latter's treatise came to our notice, but was then arranged to compare with his results, although, in addition, the limits of exposure and development were more extended than his, save in the region of solarisation.

**Experimental.**—A Beck microscope was used, the objectives being, Beck  $\frac{1}{4}$  inch, Reichart No. 8  $\frac{1}{10}$  inch, both dry systems, and for some work a Zeiss  $\frac{1}{12}$ -inch cedar-oil immersion, kindly lent by Professor A. W. Porter, B.Sc. The micrometers were a stage micrometer of  $\frac{1}{100}$  mm., an ocular calibrated on this, and, for counting the grains, an ocular micrometer divided in squares. For the ocular micrometer, with  $\frac{1}{10}$ -inch objective, No. 2 eyepiece and tube length 7.5 inches, 1 div. =  $3.43\mu$ , where  $\mu = 0.001$  millimeter.

**Emulsion Tests.**—The relation between ripening, size of grain, and sensitiveness will be discussed in the final section. Here only the points bearing on development are considered. Bellach (*loc. cit.*) drew the outline of the grains on squared paper by means of a reflecting system, then measuring the surface extension and the greatest diameter. This method gives more accurate *mean* results, and was employed as well as the micrometric method for the developed grain; but for the emulsion only the micrometer, where, with sufficient observations, the linear magnitudes can be satisfactorily determined. Preparations were made by dissolving a small piece of film in warm water, flattening in under a cover-glass, and then sealing with Canada balsam. The grains of a very thin layer thus obtained could then be examined separately. Long exposure had no apparent effect. On adding a drop of dilute developer, reduction proceeded slowly, the grain becoming opaque, and losing its symmetrical crystalline form, though not changing much in size. Fixation produced no further change. The grains in fast plates varied somewhat in size, there being, *e.g.*, in an Imperial Special Rapid plate, two species, ( $\alpha$ )  $0.0011$  mm. and ( $\beta$ )  $0.0034$  mm. The latter were flattened polyhedra, of triangular section, and definitely crystalline. In the slow plates the emulsion was practically homogeneous, the mean size of the standard Wratten Ordinary being  $0.0017$  mm. It could not be ascertained with certainty whether the grain in these was

amorphous or crystalline. The magnitudes found are of the same order as other observers.<sup>1</sup> Thus—

<i>Bellach.</i>		<i>S. and M.</i>
Apollo, Stage I.,	0'0016, "very insensitive."	Wratten Ord., 0'0017, 20 H. & D.
"	" II., 0'0023, "insensitive."	Imperial, (a) 0'0011.
"	" III., 0'0036, "very sensitive."	" (β) 0'0034, 200 H. & D.

**The Physical Nature of Halide Emulsions.**—Bellach found that in many cases the mean size of the grain diminished with careful desiccation. This points to the grain itself possessing structure, and agrees with Quincke's views as to the nature of halide emulsions.<sup>2</sup> He considers that the AgBr grains are not pure AgBr, but contain gelatine. An emulsion in which the colloid particles have flocked together forms a "foam." Liquid or jellified colloids consist of "foam" masses, with liquid or solid foam-walls, enclosing very minute or invisible chambers. In halide emulsions there is a stiff jelly containing a totally or partially solidified solution of AgBr in gelatine, in which a phase richer in AgBr has separated from a second phase poorer in AgBr but richer in gelatine.<sup>3</sup> In the foam-walls spheroids and crystals of the halide, much smaller than the measured grain, have separated. The "adsorption" of gelatine to the AgBr agrees with Eder's<sup>4</sup> results on centrifugalising pure AgBr from emulsions.

**Structure of Developed Negatives.**—By focussing on the top layer of particles, then down on the lowest observable particles, the thickness of the reduced silver layer can be measured. This apparent thickness, recorded by the micrometer head of the fine adjustment and multiplied by  $n_1/n_2$ , these being the refractive indices of the gelatine and objective systems, gives the real thickness.<sup>5</sup> The method is not very accurate, but improves with long observation and frequent focussing. The chief source of error is the presence of "fog," for even when the fog-strip is quite transparent, appreciable numbers of silver

<sup>1</sup> Bellach, *loc. cit.*      <sup>2</sup> G. Quincke, *Ann. Phys.*, 4<sup>te</sup> Flge. **V2**. 1000.

<sup>3</sup> Hardy, *Zeit. phys. Chem.*, 30. On reversible colloids.

<sup>4</sup> Eder, *Beiträge zur Photochemie*, etc., sect. 3, p. 19.

<sup>5</sup> Bellach, *loc. cit.*, p. 56.

particles may be observed. Bellach makes no mention of this, but the fog-strip should always be observed, as otherwise the value of the measurements as to thickness, etc., may be vitiated. With Wratten Ordinary emulsion, exposed and developed as described in the researches on ferrous oxalate development, the negative layer was somewhat as described by Bellach—

(a) Surface layer, particles not very numerous.

(b) Mean layer, with characteristic forms.

(c) Lower zone, with particles diminishing in size the lower they lie. This Bellach attributes to the penetration of the developer; but it will be shown later that a more potent factor is that the *most exposed grains start development first*. On ultimate development, these grains reach much the same size as the others.

TABLE 17.

*Thickness of Layer and Exposure.*

Developed in  $n/10$  ferrous oxalate at  $20^{\circ}$ . (a) for 1'0 minute; (b) for 8 minutes.

No.	Exposure.	Thickness (a).	Thickness (b).
1	0'347 C.M.S.	0'0120 mm.	0'0105 mm.
2	0'825 „	0'0107 „	0'0113 „
3	1'834 „	0'0107 „	0'0156 „
4	4'10 „	0'0112 „	0'0158 „

Each measurement is the mean of ten readings, with repeated focussings and in different parts of the film.

TABLE 18.

2'0 minutes at  $20^{\circ}$ .

No.	Exposure.	Thickness.
2	2'04 C.M.S.	0'0226 mm.
3	4'66 „	0'0223 „
4	7'75 „	0'0221 „
5	12'9 „	0'0223 „
6	27'9 „	0'0230 „
7	54'5 „	0'0255 „
8	113'0 „	0'0241 „

TABLE 19.  
10.0 minutes at 20°.

No.	Exposure.	Thickness.
1	0.1101 C.M.S.	0.0115 mm.
2	0.204 „	0.0116 „
3	0.466 „	0.0118 „
4	0.775 „	0.0139 „
5	1.290 „	0.0195 „
6	2.790 „	0.0232 „
7	—	—

The next table is for a plate developed to  $\gamma_x$ , and is somewhat suspicious, as the fog-strip, although clear, contained many reduced particles; for the high exposures with long development these would probably give too great a thickness.

TABLE 20.

No.	Exposure.	Thickness.
4	0.53 C.M.S.	0.0154 mm.
5	1.12 „	0.0177 „
6	2.06 „	0.0246 „
7	4.06 „	0.0292 „
8	8.12 „	0.0305 „

TABLE 21.

*Influence of Time of Development.*

Exposure 1.38 C.M.S., and plates developed in 0.1*n* ferrous oxalate.

Time.	Density, D.	Thickness.
2.0 mins.	0.130	0.0200 mm.
6.0 „	0.280	0.0207 „
8.0 „	0.349	0.0206 „
16.0 „	0.542	0.0203 „
$\infty$ „	0.586	0.0203 „

Hence for the thickness the following facts were ascertained :—

(a) With constant development for a short time the depth of image is independent of the exposure.

(b) With increased time of development it increases to a maximum for each exposure, after which it is constant. The density continues to increase for a moderate exposure after the thickness has reached a maximum.

(c) With prolonged development the depth increases somewhat with the exposure, a limit naturally being fixed by the thickness of the film.

These principles, ascertained for ferrous oxalate, were verified for alkaline development with hydroxylamine, quinol, and rodinal.

*Quinol*,  $C_6H_2(OH)_2$  *p*.

0.025*n* quinol in 0.05*n* NaOH, 0.05*n* Na<sub>2</sub>SO<sub>3</sub>.

TABLE 22.  
*Thickness and Exposure.*

No.	Exposure.	Density, D.	Thickness.
1	0.78 C.M.S.	0.020	0.0158 mm.
2	1.56 "	0.048	0.0214 "
3	3.12 "	0.075	0.0194 "
4	6.25 "	0.122	0.0184 "
5	12.5 "	0.202	0.0209 "
6	25 "	0.322	0.0234 "
7	50 "	0.462	0.0230 "
8	100 "	0.616	0.0244 "
9	200 "	0.760	0.0265 "

Evidently the thickness grows only slightly with the exposure for a low development.

*Time of Development.*

In 0.10*n* quinol in 0.10*n* NaOH at 20°.

Time in minutes.	E = 0.78 C.M.S.	E = 1.56 C.M.S.
	δ	δ
2.0	0.0219	0.0240
3.0	0.0239	0.0260
4.0	0.0245	0.0255
6.0	0.0259	0.0260

After a short initial period the time of development does not greatly influence the thickness.

Precisely similar results were obtained for negatives developed in hydroxylamine and rodinal, so that it does not seem necessary to give the details.

**On the Size of the Grain.**—Many discordant observations as to the influence of exposure and development on the size of the grain have been published. The following observations agree with those of Schaum and Bellach for the early stages of development, but on prolonging this the conclusions are modified. They may be expressed as follows :—

When  $\gamma$ , the degree of development, is low, the size of the grain increases with the exposure. As the time of development increases the size of the grain does also, and at  $\gamma_x$  is *independent of the exposure*.

In addition to micrometric measurements of the diameter, the mean area of the grains was obtained by drawing their outlines on squared paper by means of a reflecting system, and then measuring the surface extension. This method is tedious, and could not be applied to the smallest grains, for which the micrometer determinations are only approximate. The mean diameter by the "area" method is the mean between greatest and least, and is given to compare with the micrometer diameter. The results are the means of twenty observations, or ten for the "area" method.

TABLE 23.

*Influence of Exposure.*

Developed 2'0 minutes in 0'1*n* ferrous oxalate.

No.	Exposure.	Micro-diameter.	Area.	Mean diameter.
1	1'03 C.M.S.	0'00114 mm.	$1'23 \times 10^{-6}$ mm. <sup>2</sup>	0'00101 mm.
2	1'87     "	0'00112     "	1'45     "     "	0'00121     "
3	3'10     "	0'00124     "	1'35     "     "	0'00123     "
4	5'17     "	0'00135     "	1'82     "     "	0'00130     "
5	11'8     "	0'00140     "	1'90     "     "	0'00152     "
6	22'0     "	0'00162     "	2'10     "     "	0'00182     "

Mg. c. 920.

Mg. c. 1360.

Intensity scale with time constant.

TABLE 24.  
Developed 1·0 minute in 0·1*n* ferrous oxalate.

No.	Exposure.	Micro-diameter.
1	1·01 C.M.S.	0·0009 mm.
2	2·04 „	0·00094 „
3	4·66 „	0·00105 „
4	7·75 „	0·00114 „

Time scale with intensity constant.

It is evident that with short development the grain increases with the exposure, whether the intensity or time be varied.

For moderately high exposures and prolonged development, measurements could not be made on the plate direct, so preparations were made and the grain measured and photographed.

TABLE 25.  
Developed to  $\gamma_{\infty}$  in  $n/12\cdot5$  ferrous oxalate.

Exposure.	Density.	Micro-diameter.	Area.	Diameter.
2·04 C.M.S.	0·277	0·00145 mm.	$1\cdot94 \times 10^{-6}$ mm. <sup>2</sup>	0·00135 mm.
4·66 „	0·966	0·00150 „	2·17 „ „	0·00165 „
7·75 „	1·496	0·00137 „	1·90 „ „	0·00152 „
12·90 „	2·400	0·00156 „	2·14 „ „	0·00171 „
27·90 „	3·400	0·00149 „	1·90 „ „	0·00159 „
54·3 „	4·39	0·00151 „	2·18 „ „	0·00165 „
209·0 „	—	0·00140 „	2·03 „ „	0·00156 „

Hence, generally,  $G = \phi(\gamma, E)$ , but at  $\gamma_x$ ,  $G$  is independent of  $E$ , the exposure.

*Time of Development.*

Constant exposure 1·38 C.M.S., developed in 0·1*n* ferrous oxalate.

Time in mins.	Density, D.	Micro-diameter.	Remarks.
2·0	0·150	0·00103 mm.	
6·0	0·280	0·00124 „	
8·0	0·349	0·00157 „	
16·0	0·542	0·00160 „	Aggregates present
$\infty$	0·586	0·00167 „	„ „



These values are for the mean layer. For the lower zone the sizes for the same time were somewhat less, but generally the grain gradually increases in size with the development, reaching a maximum fixed by the original halide grain.

TABLE 26.

Exposure 0.25 C.M.S., developed in 0.1*n* ferrous oxalate.

Time.	Micro-diameter.	Remarks.
0.5 mins.	0.0004 to 0.0006 mm.	Many grains merely as just visible points, especially in lowest zone.
1.0 "	<i>circ.</i> 0.0004 "	
2.0 "	<i>circ.</i> 0.0006 "	
2.5 "	0.0005 to 0.0008 "	
5.0 "	0.0007 "	In lowest zone 0.0004 to 0.0007.
7.0 "	0.0008 "	
9.0 "	0.00085 "	
14.0 "	0.0010 "	
20.0 "	0.00104 "	
35.0 "	Up to 0.0020 "	

TABLE 27.

*Effect of Bromide.*

Developed 1.0 minute in *n*/10 ferrous oxalate ; (a) no bromide ;  
(b) 0.005*n* KBr.

Exposure.	Diameter (a).	Diameter (b).
1.01 C.M.S.	0.0009 mm.	Not visible.
2.04 "	0.00094 "	Points.
4.66 "	0.00105 "	"
7.75 "	0.00114 "	0.0008 mm.
12.9 "	—	0.00085 "
27.9 "	0.0143 <sup>1</sup>	0.00101 "
54.5 "	—	0.00123 "
113.0 "	0.0165 <sup>1</sup>	0.00145 "

This confirms Bellach's statement that addition of bromide lowers the size of the grain for the same time of development.

<sup>1</sup> From preparations.

The contrary view sometimes advanced <sup>1</sup> is probably due to a secondary effect of a very concentrated bromide with prolonged development, when complex ions are formed which "intensify" the grain. This is dealt with later. Up to a certain limit for the same time of development the size of the grain decreases as the bromide is increased; see—

TABLE 28.

Exposure 1'01 C.M.S., developed for 4'0 minutes in 0'1*n* ferrous oxalate.

No.	Concentration of KBr.	Micro-diameter.
1	0 <i>n</i>	0'00137 mm.
2	0'005 <i>n</i>	0'00114 „
3	0'010 <i>n</i>	0'00085 „
4	0'020 <i>n</i>	0'0006 „

TABLE 29.

*Bromide at Infinite Development.*

Developed to  $\gamma_{\infty}$  in 0'1*n* ferrous oxalate; 0'005*n* KBr.

No.	Exposure.	Micro-diameter.	Area.	Mean diameter.
1	2'04 C.M.S.	0'00142 mm.	$1'7 \times 10^{-6} \text{ mm.}^2$	0'00135 mm.
5	27'9 „	0'00137 „	1'9 „ „	0'00142 „
8	209'0 „	0'00172 „	2'0 „ „	0'00139 „

On comparing these figures with Table 10, it will be seen that, on infinite development, the grain attains much the same size in a bromided as in a non-bromided developer.

**Number of Grains and Exposure.**—*In the Surface Area.*—For this photo-micrographs were taken at 500 diameters and the grains counted on a given area of the negative, using a low magnification. Each value is the mean of 20 readings.

<sup>1</sup> Liesegang, *Eder's Jahrbuch*, 1897, p. 402; V. Schumann, *Photography*, 1897, p. 571.

TABLE 30.

Developed 10 minutes in 0.1*n* ferrous oxalate.

No.	Exposure.	No. per visual area.	No. per 1 mm. <sup>2</sup> film.
2	0.187 C.M.S.	17.1	192 × 10 <sup>2</sup>
3	0.310 „	16.2	181 „
4	0.517 „	18.8	211 „
5	1.18 „	17.8	199 „

For moderately long development the number of grains in the surface layer is independent of the exposure.

*In the Thickness.*—These were counted directly under the microscope with a micrometer divided in squares. The values are for 25 squares, several readings being taken over the film.

TABLE 31.

Developed 2.0 minutes in 0.1*n* ferrous oxalate.

No.	Exposure.	Density.	No. per 100 mm. <sup>2</sup> of visual field.	No. per unit volume of preparation.
1	1.38 C.M.S.	0.150	5.76	54.3 × 10 <sup>3</sup>
2	3.28 „	0.229	8.32	78.4 „
3	7.29 „	0.287	11.70	110.0 „

Mg. c. 920.

*The number of grains increases with the exposure*, being approximately proportional to the density. The unit volume is a cube of 1 mm.<sup>2</sup> area, and height equal to the depth of the layer.

As Bellach states that the number per unit volume is also constant, the experiments were repeated with as wide a range of exposure and development as was feasible. Thus in the following, 1 to 3 were below the “Schwellenwerth” of the plate.

TABLE 32.

Developed 6·0 minutes in 0·1*n* ferrous oxalate.

No.	Exposure.	No. per 100 mm. <sup>2</sup> visual.	No. per unit volume.
1	0·04 C.M.S.	2·90	$27·3 \times 10^3$
2	0·081 „	2·46	23·4 „
3	0·184 „	3·21	30·2 „
4	0·312 „	6·10	57·5 „
5	0·52 „	7·58	71·0 „
6	1·12 „	8·34	78·5 „

Mg. 1000.

At any rate, past the Schwellenwerth the number increases with the exposure ; see also—

TABLE 33.

Developed 10 minutes in 0·12*n* ferrous oxalate.

No.	Exposure.	No. per 100 mm. <sup>2</sup>	No. per unit volume.
1	0·101 C.M.S.	3·21	$30·2 \times 10^3$
2	0·204 „	7·42	70·0 „
3	0·466 „	11·35	107·0 „

TABLE 34.

Developed 6·0 minutes in 0·1*n* ferrous oxalate. Intensity scale and different emulsion.

No.	Exposure.	Density.	No. per 125 mm. <sup>2</sup> visual.	No. per unit volume.
1	0·347 C.M.S.	0·127	30·0	$23·9 \times 10^3$
2	0·825 „	0·190	51·0	40·6 „
3	1·834 „	0·339	81·0	64·5 „

The former conclusion is confirmed, viz. the number of grains increases with the exposure, and for moderately long development is nearly proportional to the density.

Bellach considers that the density-growth is due solely to the increase in the size of the grain. But it can be seen from

Table 9 that on extreme development the size of the grain is practically independent of the exposure. Yet the *density* over the range of exposure has increased from 0.277 to 4.39, or about 16 times. Since no commensurate increase in their size has occurred, the grains must have increased in number. This conclusion was further tested by preparing sections through the film. The method of paraffin embedding did not yield satisfactory results, as the film became extremely hard, and gave ragged sections. The best results were obtained by removing the developed film from the plate and rolling it up in gum-mucilage. A small portion was then frozen on an ether-spray microtome and sections cut. These gave a spiral embracing several tones, and it was easily seen that the number of grains increased with the exposure, the depth of the image but slightly. The appearance agreed with Abney's description (*loc. cit.*): "With small exposures the grains are congregated chiefly near the surface. As the exposure increases, the film behind fills up with particles and they crowd together."

TABLE 35.

*Time of Development.*Exposure 0.25 C.M.S., developed in 0.1*n* ferrous oxalate.

No.	Time.	No. per 100 mm. <sup>2</sup> visual.	Per unit volume.
1	0.5 mins.	3.35	31.5 × 10 <sup>3</sup>
2	1.0 "	3.54	33.3 "
3	2.0 "	6.10	57.5 "
4	2.5 "	6.45	62.5 "
5	3.5 "	7.20	67.8 "
6	7.0 "	8.58	80.8 "
7	9.0 "	10.03	94.5 "
8	14.0 "	10.50	99.0 "
9	20.0 "	10.40	98.9 "

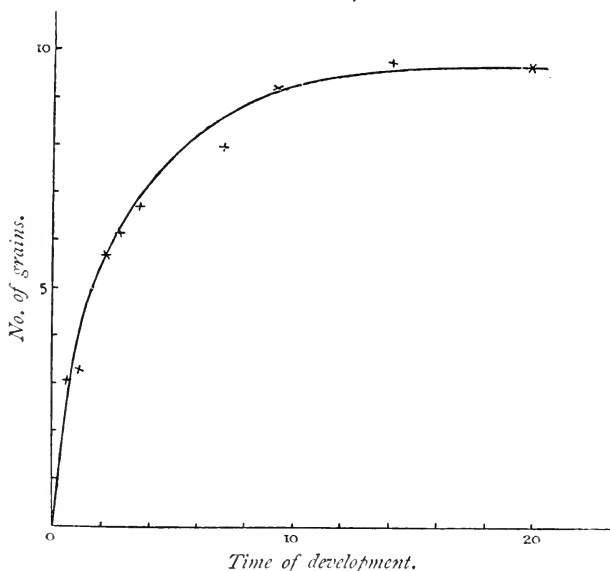
(See Fig. 17.)

The number increases rapidly at first, then more gradually, till a maximum is attained. This agrees with Bellach's results.

**Exposure through the Glass Side.**—Two standard strips were given identical exposures of 20 cms. behind the sector-

wheel and developed for 10 minutes in 0·1*n* ferrous oxalate at 15°. One was exposed through the glass side, the other from

FIG. 17.



the film side, but with a compensating glass in front. The image appeared first on the front exposed plate. Of the five tones, with the glass-side plate the three lowest appeared from the back first. The densities of the glass-side plate were much lower than those of the other.

TABLE 36.  
*Thickness of Negative-layer.*  
(a) Glass side ; (b) film side.

No.	Exposure.	Thickness (a).	D <sub>a</sub> .	Thickness (b).	D <sub>b</sub> .
1	10·0 C.M.S.	0·0204 mm.	—	0·0192 mm.	—
2	5·0 „	0·0199 „	0·110	0·0180 „	0·257
3	2·5 „	0·0188 „	0·042	0·0153 „	0·098
4	1·25 „	0·0181 „	—	0·0152 „	0·027
5	0·62 „	0·0148 „	—	0·0152 „	—

The depth is much the same for both plates ; according to Abegg, all the grains in the back-exposed plates appeared equally developed, whereas Bellach described his preparations as similar to front-exposed plates, *i.e.* uppermost zone with few and small particles, mean characteristic layer and lowest with very small particles. In our preparations the appearance agreed more with Abegg's description, the increase in size of grain being in the opposite sense to that of the film-exposed plate. The apparent divergence is probably due to the fact that Bellach used short development, 110 seconds, with a strong developer, while Abegg used prolonged stand development, more comparable with these conditions. The result shows that, other things being equal, *the grain receiving most exposure starts development first and is most reactive.*

Thus, for 1.25 C.M.S. exposure—

	Micro-diameter.	Focus.
Film-side plate	{ 0.00135 mm. . . . .	76.0
	{ 0.0008 „ . . . . .	74.0
Glass-side plate	{ 0.00106 „ . . . . .	79.5
	{ 0.00140 „ . . . . .	77.0

The number of grains was greater in the plate exposed from the air side. For 1 mm.<sup>2</sup> of film—

Air side,  $132 \times 10^3$

Glass side,  $71 \times 10^3$

Abegg and Immerwahr give  $41.0 \times 10^3$  and  $32.5 \times 10^3$ . Both the densities and the number of grains are greater for air-side plates. This is attributed by Abegg<sup>1</sup> to the prevention of free diffusion of photo-dissociated halogen. Braun's observation<sup>2</sup> may also account for it, however ; he finds that the latent image is stronger according as the oxygen pressure is increased. Possibly connected with this is the statement of Wulf,<sup>3</sup> that for the so-called photo-electric effect the sensitiveness to light increases as the potential fall of electrode to surrounding gas increases.

<sup>1</sup> Abegg and Immerwahr, *Sitz. ber. Wien. Akad.*, 1900, V. 113. 2A.

<sup>2</sup> *Zeit. wiss. Phot.*, 2. Hft. 8, 1904.

<sup>3</sup> *Ann. Phys.*, 4<sup>te</sup> Flge., 9. 946.

**Size of Grain and Nature of Reducer.**—The following table gives the mean size of grain for the same degree of development ( $\gamma$ ) at the same exposure for sundry reducers:—

TABLE 37.

Reducer.	Size of grain.
Ferrous oxalate . . .	0'0015 mm.
Hydroxylamine . . .	0'00143 „
Quinol . . . . .	0'0014 „
Rodinal . . . . .	0'00162 „

This agrees with the observation of most observers, that the size of the grain is not affected by the nature of the reducer. Certain exceptions have been brought forward by Lumière,<sup>1</sup> but in these the reducer acts as a solvent for AgBr, *i.e.*, as will be subsequently shown, it reduces the concentration of the silver ions and at certain stages acts similarly to bromides. J. Wallace<sup>2</sup> states that with certain developers there is a greater tendency to form “aggregates” or “group-particles.” This appears to occur chiefly at high exposures, where the packing is close.

**Early Stages of Development and the Physical Nature of the Process.**—Two facts brought out by the microscopic survey have an important bearing on the physical process in development. These are the practical constancy of the thickness of the image, *i.e.* the total layer in which the reaction takes place, and the increase in reactivity of the particles as the exposure is increased. The developer has to reach the whole of this layer from the solution without, and as this is the greatest path it has to traverse, it might be supposed that the rate of entry or *invasion* of the developer was the main factor in the velocity. But there are several considerations militating against this view. The invasion depends on two processes. A dry film of gelatine placed in water swells up. This *absorption* is largely

<sup>1</sup> *Zeit. wiss. Phot.*, 2. 256, 1905.

<sup>2</sup> *Astrophys. Journ.*, 1905, p. 30.



a surface-tension phenomenon, depending upon the capillary structure of the gel and similar to the wetting of powders. The rate is very rapid at first, and then falls off somewhat steeply with the time, the decrease in velocity frequently being exponential, so that if  $a_{\infty}$  be the maximum amount of water absorbable,  $a$  the amount at any time  $t$ , then—

$$da/dt = k(a_{\infty} - a)$$

The following table illustrates this :—

TABLE 38.  
1.003 gram air-dried gelatine at 20° absorbed.

$t$ in mins.	Water absorbed in grams.	$K = \frac{1}{t} \log \frac{W_{\infty}}{W_{\infty} - W}$
10.0	2.560	0.0193
20.0	4.402	0.0204
60.0	6.571	0.0185
120.0	7.069	0.0178
48.5 hours	7.103	
63.2 ,,	7.121	$K \text{ mean} = 0.0192$

Dilute solutions of electrolytes are absorbed at much the same rate as water, more concentrated ones less rapidly, while if a plate of gelatine is first soaked in water, then in a salt solution, the latter rapidly displaces the water. In fact, it sometimes happens that the amount of solution absorbed is independent of the concentration. For an interesting series of data Hurter and Driffeld's paper should be consulted.<sup>1</sup> They concluded that the rate of absorption considerably influenced the development velocity, and for example, in the case of ferrous oxalate, maintained that the velocity of development was independent of the concentration of the ferrous oxalate. Our conclusions are directly opposed to this. On the contrary, we have always found<sup>2</sup> that the velocity of development is directly proportional

<sup>1</sup> *Phot. Journ.*, 1898, **22**, 186.

<sup>2</sup> P. 64, or *Proc. Roy. Soc.*, **74**, *loc. cit.*

to the concentration. Now, since the amount of ferrous oxalate absorbed varies only slightly with the concentration, it follows that the absorption is much faster than the rate of development. A variety of results supports this principle. They may be summarised as follows:—

(a) A plate soaked in water to near its maximum swelling, develops as fast, or faster, than a dry plate.

(b) While the amount absorbed only increases slightly with the concentration, the development velocity is directly proportional to this.

(c) The temperature coefficient of development is generally greater ( $1.7 - 2.5$ ) than that of absorption ( $1.3 - 1.5$ ).

(d) The viscosity of the solution may be greatly increased without lowering the velocity of development.

(e) Hardening the film lowers the rate of absorption without altering the development velocity.

It appears that generally the mixed process of absorption and diffusion by which the developer enters the film and which may be termed the invasion or penetration is faster than development. Considering the plate as a fine network of capillary vessels, gorged with the solution, while the “grains” form a complex membrane of AgBr and gelatine, it appears probable that the rate of development depends rather on the permeation or diffusion of the reducing ion through these. Each grain develops as a more or less isolated system, only uniting to form aggregates when the packing is close. Development resembles somewhat the catalysis of  $H_2O_2$  by colloidal metals or enzymes,<sup>1</sup> the part played by convection being here replaced to some extent by the absorption. It will be seen later that this invasion does become of importance when the process of development in the film is very fast.

We have now to decide whether the rate of development depends upon the chemical velocity or a process of diffusion within the film. Before establishing any criterion as to this, we may consider the early stages of development.

**The Initial Stages of Development.**—Watkins' principle is

<sup>1</sup> Bredig, *Anorg. Fermente*, Leipzig; Sand, *Proc. Roy. Soc.*, **74**, 356, 1905; Senter, *ibid.*, **74**, 201, 1904, and *ibid.*, **74**, 566, 1905.

that for any given reducer the time of appearance of the image gives an accurate indication of the speed of working, so that any variation in concentration, temperature, etc., affecting the time necessary to reach a given density or development factor, affects the time of appearance in the same proportion. Generally—

$$T_D = WT_a$$

where  $T_D$  = time for density  $D$ ,  $T_a$  time of appearance, and  $W$  is a constant.

This rule has been usefully applied in practice for timing development, but the above statement is too wide, both experiment and theory showing that such a simple relation does not hold for many complex developing solutions when the conditions are changed. This will be illustrated later. The principle was shown to follow from the theory of the order of reactions,<sup>1</sup> which explains both the validity and the exceptions to the rule.<sup>2</sup>

The density  $\theta$ , first visible, is a small but constant fraction of the total density, being a psychological constant—a threshold value of perception. For the same exposure,  $\theta$  measures an equal fraction of the total change; for the same developer, with different exposures, it is the same fraction of the oxidation of the developer. Now, if two analogous reactions proceed to equal fractions of the total change, the correlated times are inversely as the velocity factors. Hence, if  $D_1$  and  $D_2$  be two final densities, and  $\lambda$  a fixed density less than these, while  $\delta_1$  and  $\delta_2$  are the times of appearance,  $t_1$  and  $t_2$  the respective times to reach the density  $\lambda$ , then  $t_1/\delta_1 = t_2/\delta_2 = t_n/\delta_n = \text{constant } W$ , whose numerical measure is proportional to the Watkins multiple, and depends only on the velocity function. The general theorem is only true for simple reactions, and does not hold for “graded,” “catalysed,” and so forth. *The same limitations hold for development*, and the coupling of simultaneous reactions, or initial disturbances, varying with different reducers, are

<sup>1</sup> Ostwald, *Lehrbuch*, 2nd edit., 2. 236.

<sup>2</sup> *Proc. Roy. Soc.*, 1905, 76A. 217.

sufficient to account for the wide variation of the Watkins multiple, as well as its occasional inconstancy with the same developer. Deviations may occur for such a small fraction of the total change and yet the development function remain much the same.

The limiting conditions for experimental accuracy are the same for all "time of appearance" methods in chemical dynamics.<sup>1</sup> The time must not be so short that the limiting error of measurement seriously affects the result, nor so long as to cause doubt as to the exact moment. The observations are made in a dark room, using plenty of a steady reddish light, as subsequent fogging is generally immaterial. The timing may be carried out with a stop-watch marking fifths of a second, except when rapidly following determinations are necessary. An apparatus for these is described subsequently. Taking the mean of several measurements, and using for comparison only those made at one period, the method is accurate to about 2 per cent. For ferrous oxalate, it was shown in the previous chapter that from  $n/5$  to  $n/50$ , the "time of appearance" is inversely as the concentration, and hence the initial velocity directly proportional to this. The effect of temperature on the initial and mean velocity was measured, and Van't Hoff's equation,<sup>2</sup>  $\frac{d \log K}{dT} = \frac{A}{T^2}$  for A constant and integrated,

$\log K = -\frac{A}{T} + C$ , where T is the absolute temperature,

A and C constants, was found to represent the results very fairly, in the form  $\log K = -1806/T + 7.60$  from  $0^\circ\text{C.}$  to  $30^\circ\text{C.}$  The temperature coefficient for  $10^\circ$  was 1.7. Further, it was found that hardening the gelatine in a solution of formalin which rendered it insoluble in boiling water, had no influence on the development velocity, as we should have expected if the penetration of the developer were of great importance.

**"Penetration" of Developer.**—By this we understand the time required for the developer to pass through the complete reaction layer  $\delta$ . It was studied as follows. If plates are

<sup>1</sup> Ötlingen, *Zeit. phys. Chem.*, **30**, 20.

<sup>2</sup> *Kgl. Svenska Vid. Hdl.*, **21**, 17, 1885.

exposed through the glass side, the image will lie nearer the glass, and we may expect it to appear—

(a) On front first if the penetration of the developer count most.

(b) On the back first if the greater reactivity of the more exposed particles be the predominant factor.

A strip of Ilford ordinary film was exposed, cut up, and developed in  $n/10$  ferrous oxalate at  $15^{\circ}\text{C}$ . The values of  $T_a$  are the means of four experiments.

TABLE 39.

Exposure.	$T_a$ , film side.	$T_a$ , glass side.
Ilford film.		
300 C.M.S.	40'3 secs.	45'3 secs.
60    ,,	54'6    ,,	52'6    ,,
10     ,,	72'4    ,,	63'0    ,,
Wratten Ordinary.		
300 C.M.S.	94'2    ,,	90'4    ,,

There is not much difference in the times, but at low exposures the back appears before the front; but as the exposure increases, the developer being the same, the two times become the same, and eventually the image appears on front first. This was confirmed on plates exposed in the sensitometer. Plates given the same exposure from the front always show the image on front first, the relative difference in time being somewhat greater, the absolute value of  $T_a$  always less. The foregoing phenomena may be explained by the following considerations drawn from the microscopy of the image:—

(a) The absolute thickness of the layer of developable particles increases but slightly with the exposure.

(b) Reckoning down through the layer from the exposed side, the reactivity of each layer of grains diminishes through the depth. *The slope* of this reactivity gradient then depends upon the exposure.

(c) The penetration is complete at a very early stage of development, but as the developer reaches the lowest layers, its concentration will be diminished somewhat by diffusion and oxidation by developable AgBr. There will therefore be a concentration gradient through the film.

(d) Then in the case of exposure from the film side, the two gradients will be in the same sense and will reinforce each other; for exposure from the back they will be opposite in direction, and the front layers or the back may appear first according as one factor or the other predominates. This result is in agreement with the microscopic deduction that, *ceteris paribus*, the more exposed grains possess the greater reactivity, and start development first.

As to the absolute time required for the developer to penetrate the thickness of the film, an estimate can be obtained as follows: With an Ilford film, the  $\gamma$ ,  $t$  curve of which was known, the *least* time of appearance at the back for any exposure through the back was about ten seconds with  $n/10$  ferrous oxalate at  $15^{\circ}$ . Now, under these conditions the half-period of development, *i.e.* for  $\gamma_x/2$ , was 5.0 minutes. Hence any initial error due to incomplete penetration is not of a very large order, and we shall see that there are reasons for assuming a chemical induction greater than this diffusion induction.

**Temperature and Development Velocity.**—Bodenstein<sup>1</sup> and Senter<sup>2</sup> have indicated the value of the temperature coefficient for  $10^{\circ}$  as a criterion in heterogeneous reactions. For chemical reactions in homogeneous solution the value is generally about 2-3,<sup>3</sup> while Brunner found 1.5 for the rate of solution of benzoic acid in water; for diffusion processes we should expect a value of 1.5 about, and not varying much for different reactions.

The following table gives some results for development, those with alkaline development being given in advance of the section on this:—

<sup>1</sup> *Zeit. phys. Chem.*, 1904, **49**, 42.

<sup>2</sup> *Roy. Soc. Proc.*, 1905, **74**, 214.

<sup>3</sup> Van't Hoff, *Vorles*, **I**, p. 225.



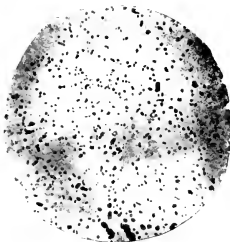
# DESCRIPTION OF PLATE.

Figs. I. to IV. are from preparations as described on p. 70, etc.

Fig. V. was photographed directly from the plate, and shows the grains *in situ*; the large "aggregates" are as much due to superposition of grains as to physical fusion.



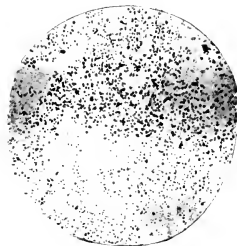
I



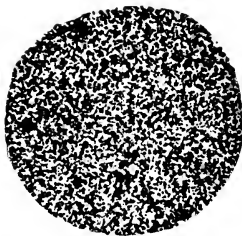
II



III.



IV



V.

I., II. for  $\gamma$ , 209 C.M.S. and 2 C.M.S.

III, IV. ditto ditto ditto  
In N/200 KBr. Mg., C. 900  
(see Tables 25 and 29, Chap.  
II.).

V. 1:38 C.M.S., dev. 10 minutes.  
In N/10 FeOx at 20° C. Mg., C. 900.



TABLE 40.

Reducer.	Emulsion, A.	B.	C.
Ferrous oxalate . . .	1'60	1'90	1'70
„ citrate . . .	1'52	—	—
„ fluoride . . .	1'54	—	—
Hydroxylamine . . .	—	—	2'00
Hydroquinone . . .	—	2'20	2'80
P. amido-phenol . . .	—	—	1'50
Metol . . .	—	—	1'25
Pyrocatechin . . .	—	2'80	—

The temperature-coefficient frequently passes the value to be expected from the diffusion theory. But in the case of development we must be cautious in applying the criterion. The value varies with different emulsions and reducers, and there are other considerations. Beside the increase in diffusivity (mobility) of reducing molecule, we must also consider (a) alteration of resistance to permeation in film; (b) in complex developing solutions, alteration of the concentration of reducing ion by changing the chemical equilibrium. Under these conditions *a high temperature coefficient in development does not necessarily imply that the velocity is that of the chemical reaction.*

This being the case, it is necessary to establish some other criterion. Consider a general equation typical of development;  $-Ag + R'' = Ag(\text{met.}) + R'$ .

If this reaction be reversible, then the addition of the oxidation product should affect the velocity of development, if this depend upon the chemical reaction. So also the addition of the halogen ion should affect the velocity, since we have  $Ag \times Br = \text{constant}$ . A study was made, therefore, of the reversibility of development and the action of soluble bromides, which exert a well-known retarding influence.

## CHAPTER III

### THE REVERSIBILITY OF DEVELOPMENT AND THE ACTION OF SOLUBLE BROMIDES

THAT development is essentially a *reversible* chemical reaction has been frequently maintained both *a priori* from theoretical considerations, and also as a conclusion drawn from some of the phenomena of photographic practice. It was brought forward as fundamental by H. E. Armstrong,<sup>1</sup> both for wet and dry-plate development; and again expressed by Hurter and Driffield.<sup>2</sup> These writers concluded that the so-called "restraining" action of soluble bromides is due to their being reaction-products of a reversible reaction.<sup>3</sup> On the other hand, Abegg<sup>4</sup> pointed out that this action was qualitatively explicable by the isohydric depression in concentration of the silver ion by a salt with the same anion. He has since developed his views further so as to include the reversibility of the reaction.<sup>5</sup> In spite of the importance of the question for photographic theory, but little experimental work has been done. Friedländer<sup>6</sup> has shown that large quantities of ferric oxalate retarded development, measuring the densities of plates exposed in a Scheiner sensitometer. The writers found that negatives were completely bleached in mixtures of ferric oxalate and potassium bromide, while the addition of ferric oxalate was found to

<sup>1</sup> *Brit. Journ. of Phot.*, **39**, 277.

<sup>2</sup> *Phot. Journ.*, 1898, **22**, 360.

<sup>3</sup> Luther, *Chem. Vorgänge in der Phot.*, 1900, 35 *et seq.*

<sup>4</sup> *Arch. wiss. Phot.*, 1900, ii, 76.

<sup>5</sup> *Eder's Jahrbuch*, 1904, 1.

<sup>6</sup> *Phot. Corr.*, 1902, 252.

produce a retardation in development. The following investigation may be regarded as consisting of two parts: (I.) the experimental attainment of an equilibrium in development; (II.) the influence of the chemical reactions on the velocity of the process.

**PART I. The Chemical Reactions in Development.**—Chemically considered, development is a reduction process,<sup>1</sup> and in terms of the ionic theory may be formulated as follows:—



In the case of ferrous oxalate, the molecular condition in the solution of which has been investigated by the writers,<sup>2</sup> this becomes—



Probably in the presence of excess of oxalanion, the ferric complex is to be formulated  $\text{Fe}(\text{C}_2\text{O}_4)_3'''$ ; <sup>3</sup> but the adjustment  $\text{Fe}(\text{C}_2\text{O}_4)_2' + \text{C}_2\text{O}_4'' \rightleftharpoons \text{Fe}(\text{C}_2\text{O}_4)_3'''$  will not affect the main reaction. Furthermore, the concentration of the silver ion will be determined by that of the free halide ion. For bromide plates,  $\text{Ag}^{\cdot} + \text{Br}' \rightleftharpoons \text{AgBr} \rightleftharpoons \text{AgBr (solid)}$ . From these equations we can formulate the equilibrium condition. In presence of excess of oxalate, we are justified by spectro-photometric results <sup>4</sup> in assuming all the iron to be present as complex ion. Hence for convenience the symbols  $\text{Fe}''$  and  $\text{Fe}'$  are used, and from the equation  $\text{Ag}^{\cdot} + \text{Fe}'' \rightleftharpoons \text{Ag (met.)} + \text{Fe}'$  we have  $\frac{[\text{Fe}''][\text{Ag}^{\cdot}]}{[\text{Fe}']} = \text{constant}$ , the concentration of metallic silver in presence of solid silver being constant. Again, from  $\text{Ag}^{\cdot} + \text{Br}' \rightleftharpoons \text{AgBr} \rightleftharpoons \text{AgBr (solid)}$ , we have  $[\text{Ag}^{\cdot}][\text{Br}'] = \text{constant}$ , which gives  $\frac{[\text{Fe}'']}{[\text{Fe}'][\text{Br}']} = \text{constant, K.}$

**Experimental Determination of the Equilibrium Constant.**—In the first method used, plates of known area and

<sup>1</sup> Cf. G. Bredig, *Eder's Jahrb.*, 1895, 42.

<sup>2</sup> *Chem. Soc. Trans.*, 1905, 87. 189.

<sup>3</sup> *Trans.*, *loc. cit.*; also Rieger, *Zeit. Elektrochem.*, 1901, 7. 170.

<sup>4</sup> *Chem. Soc. Trans.*, *loc. cit.*

density were placed in a mixture of aqueous ferric oxalate and potassium bromide, the silver bromide formed fixed out and determined by difference photometrically when the bleaching had ceased. From this the change in concentration of the components could be calculated, and hence  $K$ , the equilibrium constant. Thus, if the original density be  $D_0$  and the final density  $D$ , if  $m$  and  $n$  be the factors for converting "densities" into concentrations of iron and bromide respectively, and  $A$  the plate area, then  $\frac{m \text{ or } n (D_0 - D)A}{100}$  is the change in concentration. Calling this  $c$  or  $c'$ , we get—

$$\frac{[\text{Fe}'' + c]}{([\text{Fe}' - c] ([\text{Br}' - c'])} = K$$

However, this method only gave an upper limit to the equilibrium constant, as near the equilibrium point the reaction proceeds with extreme slowness, and atmospheric oxidation, though reduced as far as possible, then introduces large errors. A more successful method was obtained by "balancing," and gave superior and inferior limits to the constant as follows: All reaction mixtures for which the ratio  $[\text{Fe}''([\text{Fe}']^{-1} ([\text{Br}']^{-1})$  is above a certain ratio will be reducers, while those for which it is below this value will be oxidisers. Test strips were made by giving plates a liberal exposure in the sensitometer, and leaving a part unexposed. When placed in the reaction-mixture, development either took place or was inhibited. By narrowing the limits on either side, upper and lower values for  $K$  were obtained. The reverse balancing method in which equilibrium is attained from the opposite side consists in determining the concentrations which just bleach or fail to bleach the silver of a negative. The solutions were made with boiled air-free water, and slightly acid. Control experiments showed that the oxidation error was slight. The iron was used in the form of standardised ferrous and ferric sulphate solutions, added to potassium oxalate solution. For brevity only the limiting concentrations are given.

TABLE 41.

Volume in c.c.	No. of grm.-mols. ferrous iron.	Gram-mols. ferric iron.	Gram-mols. of bromide.	K + = developer. - = oxidizer.	
25	0'000092	0'00321	0'0101	710	+
25	0'000092	0'00350	0'0101	650	-
25	0'000092	0'00374	0'0101	600	-
Value lies between 710 and 650.					
25	0'000046	0'00160	0'0101	710	+
25	0'000046	0'00165	0'0101	690	-
Value lies between 710 and 690.					
25	0'000036	0'00180	0'0101	650	-
25	0'000036	0'00130	0'0101	690	+
Value lies between 690 and 650.					

Hence, varying the concentration of the ferrous iron from 92 to 36, the value of K is constant at about 670, 700, 680, mean being 683.

**Effect of Bromide.**—The above experiments show that at 25 c.c. in  $n/25$  bromide, the ferric iron must be 36 times the ferrous, in order that the system may be in equilibrium. The other factors, the bromide and the volume, were also varied.

TABLE 42.

Volume in c.c.	Mols. of Fe <sup>''</sup> .	Mols. of Fe <sup>'</sup> .	Mols. of bromide.	K.	Remarks.
25	0'000036	0'000504	0'00255	700	+
25	0'000036	0'000525	0'00255	672	-
Value lies between 700 and 672.					
25	0'000036	0'00180	0'00101	650	-
25	0'000036	0'00130	0'00101	690	+
Value lies between 690 and 650.					
25	0'000036	0'00264	0'000505	674	-
25	0'000036	0'00258	0'000507	690	+
Value lies between 690 and 674.					

Hence, varying the concentration of the bromide from  $n/10$  to  $n/50$ , one obtains  $K = 686, 670, 682$ ; mean, 680.

**Effect of Dilution.**—An equilibrium mixture at 25 c.c., when diluted to 100 c.c., is no longer in equilibrium; such mixtures continue the development of a plate, and by the bleaching method the following values were obtained at 100 c.c.:—

TABLE 43.

Volume in c.c.	Mols. of ferrous.	Mols. of ferric.	Mols. of bromide.	K.	Remarks.
100	0'000115	0'00415	0'00404	685	+
100	0'000115	0'00423	0'00404	673	—
100	0'000115	0'00436	0'00404	653	—

Hence the equilibrium concentration of iron is directly proportional to the volume between 25 c.c. and 100 c.c.

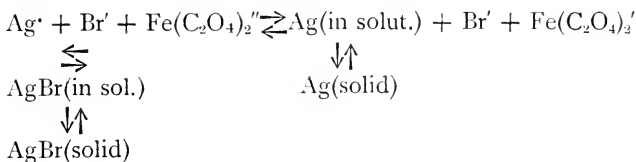
The above experiments obtained by development and by the bleaching control establish the existence of an equilibrium in development with ferrous oxalate, and show it to be defined

by the equation  $\frac{a \times v}{b \times c} = K$ , where  $a$ ,  $b$ , and  $c$  are the gram-molecules of ferrous, ferric iron, and bromide respectively, while  $v$  is the volume of the solution; the measurements were made at 18° to 20°.

Since the equilibrium concentration of iron appears to be inversely proportional to that of the bromide, we can calculate its value for normal development with bromide at, say,  $n/1000$ .  $K$  is found as 680. Correcting this for the ionisation of the bromide gives  $680/0'90 = 755$ . Hence at  $n/1000$  Br', the concentration of ferric iron would have to be some 1500 times that of the ferrous to bring development to a standstill. Under normal conditions the reaction can proceed very far in the direction of development. This explains why the addition of large quantities of ferric oxalate is required to retard development. The relation between the equilibrium in development and the free energy of the reaction is treated later under alkaline development.

PART II. On the Influence of the Chemical Reactions on the Velocity of Development.—It was already found<sup>1</sup> that the influence of bromide on the rate of development was not simple, as of concentration, but the main effect was the formation of an induction-period which depended both on the exposure received and the bromide concentration.

The course of chemical reactions in heterogeneous systems is likely to be very complicated, unless one of the processes is relatively far slower than the others. Nernst's theory<sup>2</sup> assumes that diffusion determines the velocity; but this is not always the case, and other conceptions are then necessary. A very comprehensive theory of reaction velocity in heterogeneous systems has been advanced by M. Wilderman,<sup>3</sup> in which, however, diffusion is not considered. On the basis of this theory it can be shown that, neglecting the "invasion" of the developer, the course of the reaction is still represented by much the same function of the density of the image, while the existence of the reverse reaction can give rise to an induction period, which the subsequent experiments demonstrate.<sup>4</sup> The process of development may be formulated as follows:—



The various processes may be considered as follows. For the rate of solution of the silver bromide we have—

$$\begin{array}{c}
 \text{AgBr} \rightleftharpoons \text{AgBr}(\text{in solution}) \\
 \left( \frac{dx}{dt} \right) = K(\text{C}_0 - \text{C})\text{S}
 \end{array}$$

where  $\text{C}_0$  = saturation or equilibrium concentration,

$\text{C}$  = concentration at time  $t$ ,

$\text{S}$  = surface of silver bromide.

<sup>1</sup> *Roy. Soc. Proc.*, 1905, **74**, 462.

<sup>2</sup> *Zeit. phys. Chem.*, 1904, **47**, 56.

<sup>3</sup> *Zeit. phys. Chem.*, 1899, **30**, 341.

<sup>4</sup> See *Chem. Soc. Trans.*, 1905, **87**, 1317.

For AgBr in solut.  $\rightleftharpoons \text{Ag}^{\cdot} + \text{Br}^{\cdot}$

$$\left(\frac{dx}{dt}\right)' = K'(C - C_{\text{Ag}^{\cdot}} C_{\text{Br}^{\cdot}})$$

For the reduction—

$$\left(\frac{dx}{dt}\right)'' = K''[\text{Fe}''[\text{Ag}^{\cdot} - K'''[\text{Fe}'[\text{Ag}$$

And for the precipitation or solution of metallic silver—

$$\left(\frac{dx}{dt}\right)''' = K^{\text{iv}}S'(C_0' - C')$$

Silver is precipitated or dissolved according as its concentration is above or below saturation. But if  $S'$ , the surface, be nil, metallic silver will still be precipitated at a certain concentration, so that Wilderman introduces an "instability-constant," say  $I$ , and we have—

$$\left(\frac{dx}{dt}\right)''' = K^{\text{iv}}(S' + I)(C_0' - C')$$

Assuming a certain state of balance among these simultaneous reactions, a general equation may be obtained integrable under certain conditions.<sup>1</sup> We have further to consider the supply of reducer by diffusion, treated previously—

$$-\frac{d\text{Fe}''}{dt} = \frac{a\Delta}{\delta}(D_{\infty} - D)$$

It is obvious that unless one action be entirely predominant by reason of its slowness, the velocity-curve will be complicated, as in graded homogeneous reactions.<sup>2</sup>

**Experimental.**—The action of bromide on the characteristic plate-curve has been determined with ferrous oxalate for concentrations of bromide from  $n/200$  to  $n/10$ , the time of development being varied from two minutes to two hours, while the range of exposure was 1—256. Two tables are given from these for four and six minutes' development. The plates were the standard ones described at the start.

Each plate was given 100 c.c. of a developer composed as

<sup>1</sup> *Trans. Chem. Soc., loc. cit.*

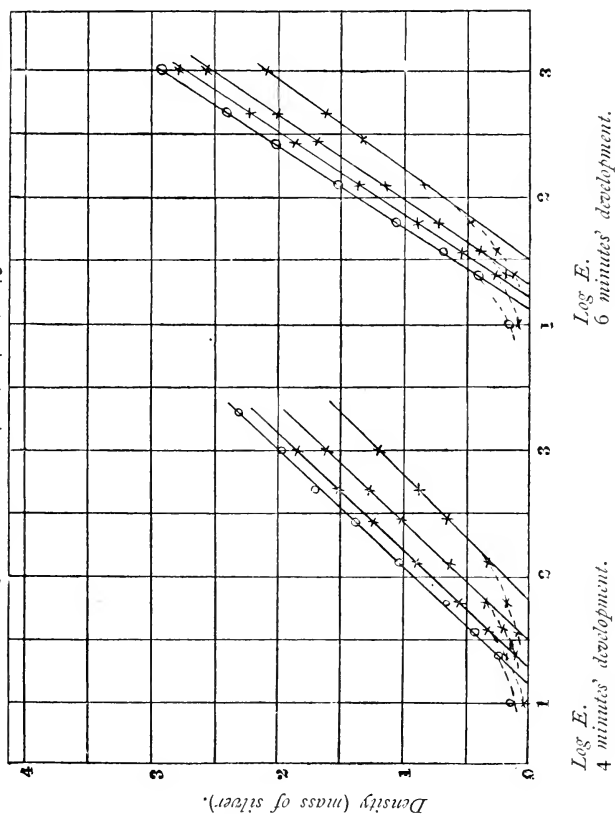
<sup>2</sup> J. W. Mellor, *Chemical Statics and Dynamics*, 1904, p. 95.



follows, the development being carried out in the manner previously described :—

$$\left. \begin{array}{l} 8.0 \text{ c.c. molar FeSO}_4 \\ x \text{ c.c. } ,, \text{ KBr} \\ \text{to } 100 \text{ c.c. with molar K}_2\text{C}_2\text{O}_4 \end{array} \right\} \text{Fe}'' = n/12.5$$

FIG. 18.—Effect of bromide on the characteristic plate curve: for concentrations of bromide, 0,  $N/200$ ,  $N/100$ ,  $N/50$ .



In the two following tables the logs of the exposures are given on an arbitrary scale, putting  $\log E_9 = 1.00$ . A plate was always developed for the same time to obtain the true inertia.

TABLE 44.

Time of development, 4.0 minutes ;  $D$  = density ;  $n$  = concentration of bromide.

Log E.	$D_0$ .	$D_n/200$ .	$D_n/100$ .	$D_n/50$ .
3.313	2.340	—	—	—
3.012	2.000	1.857	1.655	1.179
2.72	1.822	1.562	1.295	0.895
2.42	1.454	1.250	0.971	0.608
2.14	1.068	0.952	0.648	0.380
1.80	0.713	0.590	0.368	0.195
1.575	0.446	0.335	0.193	0.097
1.36	0.261	0.200	0.101	—
1.00	0.056	0.030	—	—
log $i$	1.15	1.30	1.50	1.80
$\gamma$	1.11	1.10	1.07	1.08

TABLE 45.

6.0 minutes' development.

No.	Log E.	$D_0$ .	$D_n/200$ .	$D_n/100$ .	$D_n/50$ .	$D_n/25$ .
2	3.012	2.902	2.760	2.605	2.130	1.629
3	2.72	2.501	2.292	2.027	1.706	1.270
4	2.42	2.080	1.832	1.611	1.301	0.938
5	2.14	1.603	1.410	1.114	0.948	0.666
6	1.80	1.086	0.865	0.705	0.544	0.364
7	1.575	0.666	0.548	0.404	0.306	0.205
8	1.36	0.413	0.290	0.208	0.150	0.092
9	1.00	0.126	0.081	—	—	—
	log $i$	1.10	1.20	1.35	1.50	1.60
	$\gamma$	1.51	1.51	1.51	1.40	1.10

On very prolonged development, identical values for log  $i$  and  $\gamma$  were obtained with no bromide and in  $n/50$  bromide ; the results of all the experiments up to  $n/50$  bromide are given in the next table.

TABLE 46.

log  $i$  for no bromide reduced to 1'00.

Time in mins.	$n/_{\infty}$ .	$n/_{200}$ .	$n/_{100}$ .	$n/_{50}$ .	$\gamma$
2'0	1'00	(1'81)	—	—	0'59
3'0	1'00	1'45	1'63	—	1'00
4'0	1'00	1'13	1'305	1'52	1'10
5'0	1'00	—	1'20	—	1'40
6'0	1'00	1'09	1'225	1'36	1'51
8'0	1'00	1'067	—	1'215	1'80
12'0	1'00	1'042	1'09	1'122	2'00
$\infty$	1'00	1'00	1'00	1'00	3'40

The experiments show that up to  $n/50$  bromide the development factor  $\gamma$  is unaltered, but log  $i$  and  $i$ , the inertia, are raised. That is to say, the depression of D, the density, is constant over a certain range. Above  $n/50$  the effect on log  $i$  is relatively less, while  $\gamma$  is now lowered so that there is no longer a period of constant depression. This and the consequent raising of log  $i$  becomes less as the time of development is increased, and on ultimate development disappears. In consequence a definite "regression of the inertia" takes place, as shown in Table 46. The shift  $\Delta$  log  $i$  from the data obtained appears to be directly proportional to the concentration of the bromide and inversely proportional to the time of development, as will be seen from Table 47.

TABLE 47.

 $P = \Delta \log i \times \text{time of development.}$ 

Time, $t$ .	P for $n/_{200}$ .	P for $n/_{100}$ .	P for $n/_{50}$ .
4'0 mins.	0'52	1'20	2'08
5'0 "	—	1'00	2'16
6'0 "	0'54	1'35	1'72
8'0 "	0'53	—	—
12'0 "	0'50	1'08	1'50

It is possible from these data to give correction-formulæ for the effect of bromide on the exposure and development curves. For the exposure—

$$D = \gamma \log \frac{E}{i} - \frac{114n}{t}$$

where  $n$  is the normality of the bromide,  $t$  the time of development. The effect on the development curve is similarly obtained. Without bromide,  $D = D_{\infty}(1 - e^{-K'})$ , and the addition of bromide results in the correction term,  $\frac{K'[\text{Br}']}{t}$ , so we have—

$$D = D_{\infty}(1 - e^{-K'}) - \frac{K'[\text{Br}']}{t}$$

**Periods of Over- and Under-exposure.**—The linear portion of the exposure curve is, for certain photographic reasons,<sup>1</sup> called the period of correct exposure; whilst in this region the density depression is constant, it is not so for the other portions of the curve. When the range of illumination is greatly extended, it is found that the depression increases at first, becomes approximately constant over a certain range, and then decreases. Curves and tables exhibiting this have been given elsewhere, and it appears that the parallelism of the curves applies rather to the  $\log E$  axis, *i.e.* for the same density on each curve  $\Delta \log E$  is constant. Consequently for the period where  $D$  is proportional to  $\log E$ ,  $\Delta D$  is constant. It will be seen later that this effect is in agreement with the “times of appearance” result, where it is shown that the “retardation time”  $\times \log E$  is constant.

**Influence of Bromide on the Velocity of Development.**—From the data obtained and the results in Table 46, the velocity curves were constructed for exposures from  $\log E = 1.36$  to  $3.01$ , about the range for which the equation  $D = \gamma (\log E - \log i)$  is valid. The three following are given:—

<sup>1</sup> Hurter and Driffeld, *Journ. Soc. Chem. Ind.*, 1890, 9, 455.

TABLE 48.

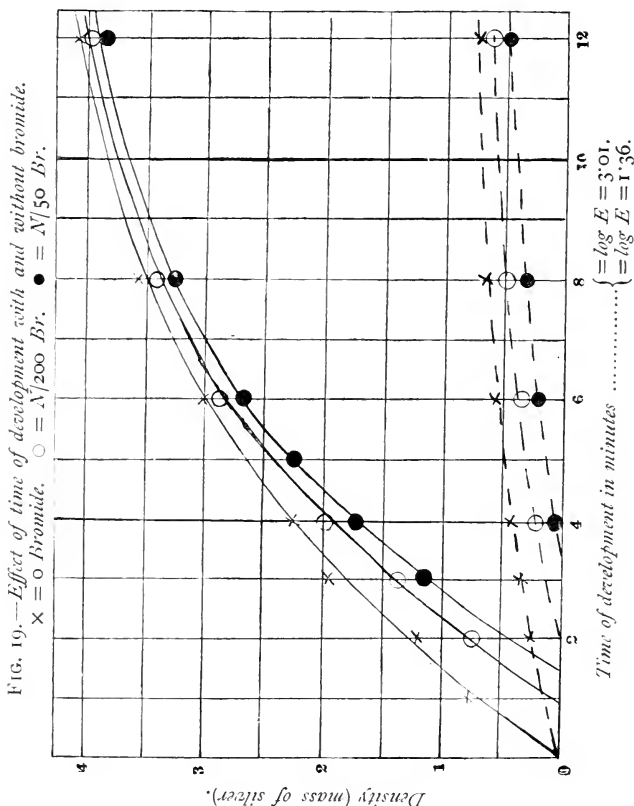
Conc. of bromide.	Log E.	Time in minutes.							
		2.	3.	4.	5.	6.	8.	12.	∞.
0	3'01	1'186	2'01	2'23	—	3'04	3'62	4'02	6'84
0'005 <i>n</i>	3'01	0'708	1'39	2'06	—	2'90	3'50	3'94	6'84
0'010 <i>n</i>	3'01	—	1'20	1'89	2'54	2'70	3'39	3'84	6'84
0	2'14	0'673	1'14	1'265	—	1'72	2'08	2'28	3'88
0'005 <i>n</i>	2'14	0'195	0'52	1'11	—	1'58	1'93	2'20	3'88
0'010 <i>n</i>	2'14	—	0'33	0'93	1'31	1'48	1'82	2'10	3'88
0	1'36	0'223	0'36	0'40	—	0'54	0'65	0'72	1'225
0'005 <i>n</i>	1'36	—	—	0'25	—	0'41	0'53	0'64	1'225
0'010 <i>n</i>	1'36	—	—	0'06	0'224	0'21	0'42	0'54	1'225

From the table and curve, the nature of the retardation produced by bromide is obvious. *Whilst with no bromide every density grows proportionately from the start, bromide causes an initial induction or retardation-period, the length of which depends both on the exposure and the bromide concentration.* It seems probable that this induction, which was indicated by the preliminary theoretical discussion, is primarily due to the time required for the first precipitation of metallic silver. Theories as to the mechanism of development <sup>1</sup> have generally assumed that the reduction of the silver ion leads to the formation of a supersaturated solution of metallic silver, which is then deposited locally according to some function of the exposure. Now, in the earlier discussion of reversibility it was assumed that equilibrium was reached in the presence of solid metallic silver, the concentration of which was then constant. Otherwise, if the silver solution has to reach a meta-stable limit, the reverse reaction is greatly accelerated, its velocity being given by  $-dx/dt = K[Ag[Fe''']$ . The only quantitative experiments bearing on the meta-stable limit are those of Morse and Pierce,<sup>2</sup> with silver chromate in gelatine; they found that the

<sup>1</sup> Ostwald, *Lehrbuch*, 1893, ii. I., 1078; Abegg, *Arch. wiss. Phot.*, 1899, i. 15; K. Schaum, *ibid.*, 1900, ii. 9.

<sup>2</sup> *Zeit. phys. Chem.*, 1904, 45. 600.

solution could, in the absence of the solid phase, contain silver chromate up to 150 times the saturation concentration. It will be seen how greatly the reverse reaction is accelerated under these conditions.



### The Function of the "Latent Image" in Development.—

Reference has been made to Wilderman's "instability constant" of supersaturated solutions, a conception which is only a modification of Ostwald's meta-stable limit. The photographic latent image acts by inducing the precipitation of silver

before this limit is reached. This question and the nature of the "latent image" will be discussed later. But we may note that the microscopic survey showed that the halide *grain* is the unit to be considered in development, and both microscopic and dynamical experiments showed that the more exposed grains started development first, *i.e.* were more reactive. The instability of the silver solution formed will be therefore a steady function of the exposure. We may now picture the process of development somewhat more definitely. In the first act, a supersaturated solution of silver is formed, the time depending chiefly on chemical velocities. When the concentration has reached a certain limit, depending upon this instability, and hence upon the exposure, metallic silver is deposited; by the consequent lowering of the reverse reaction, the total velocity is accelerated, the silver acting auto-catalytically in the sense of the silver germ theory of development, *but only for the individual grain*. Such auto-catalysis in heterogeneous solutions is already well known, as in the decomposition of the thiosulphate by acids,<sup>1</sup> or in the thermal decomposition of the antimony hydride.<sup>2</sup> It then appears that the chemical velocity is so accelerated shortly after the first decomposition of metallic silver, that it becomes fast compared with the diffusion of the reducer, so that in the later stages of development bromide has but little influence. This agrees with the trend of the curves and with the fact<sup>3</sup> that the addition of bromide after the commencement of development has but little effect. In this period the rate of development depends chiefly upon the diffusion of the developer to the affected halide grain, which process is represented under certain conditions by the equation  $1/t \log D_{\infty}/D_{\infty} - D = K$ . One may allow to some extent for this initial induction by writing this,  $\log D_{\infty}/D_{\infty} - D = K(t - \alpha)$ , and we have to find how  $\alpha$ , the initial induction, depends on the exposure and the bromide concentration. This may be done in part by graphic extrapolation of the velocity-curves to the time-axis.

<sup>1</sup> Foussereau, cited by Ostwald, *Lehrbuch*, 2nd edit., II. 300.

<sup>2</sup> Bodenstein, *Zeit. phys. Chem.*, 1904, 49. 42.

<sup>3</sup> *Phot. Journ.*, 1904, 290.

But besides the uncertainty of this procedure, the examination of the "time of appearance" is at hand, which is a measure of the velocity at an early stage. The effect of bromide on this has therefore been determined both for varying exposure and strength of bromide.

**Effect of Bromide on  $T_a$ .**—Owing to the extended range of concentration employed, in constructing a curve the values of  $T_a$  were plotted against the *logarithm* of the bromide concentration, and it was then found that for a considerable range this curve was nearly linear, the relation failing about  $n/20$ , the retardation then increasing more rapidly. In the table  $V = 1/T_a$ , and the calculated values are got from  $V \log_{10} [\text{Br} = \text{constant}, A]$ .

TABLE 49.

$T_a$  mean value in seconds.

Concentration.	Log [Br $\times$ 10.	A.	$T_a$ .	V observed.	V calculated.
0.0	—	—	14.8	6.57	—
0.0005 normal	0.699	3.23	21.6	4.62	5.12
0.0010 "	1.000	3.51	28.5	3.51	3.58
0.0015 "	1.176	3.70	31.6	3.16	3.05
0.0020 "	1.301	3.90	33.2	3.01	2.75
0.0025 "	1.398	3.64	38.5	2.60	2.56
0.0040 "	1.602	3.44	46.4	2.15	2.23
0.0050 "	1.699	3.50	48.5	2.06	2.11
0.0100 "	2.000	3.70	53.5	1.87	1.79
0.0150 "	2.176	3.72	58.1	1.72	1.65
0.0200 "	2.301	3.80	60.5	1.65	1.56
0.0250 "	2.398	3.72	64.5	1.55	1.49
0.0400 "	2.602	3.28	79.6	1.26	1.38
0.0500 "	2.699	3.25	84.2	1.19	1.28
0.1000 "	3.000	—	101.8	0.98	—

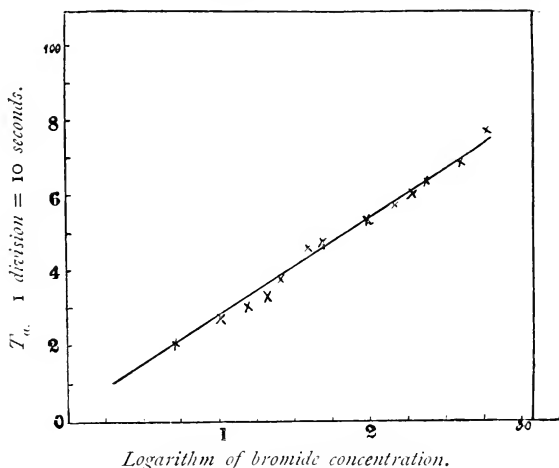
$$A = 3.58.$$

Similar results were obtained on other plates, and it appears that up to about  $n/25$  bromide, the time of appearance is a



linear function of the logarithm of the bromide concentration, that is,  $T_a = a \log [\text{Br} + b]$ , where  $a$  and  $b$  are constants,  $b$  depending upon the exposure, and expressing the value of  $T_a$ , when  $[\text{Br}]$  is zero,  $a$  a function of the exposure and the plate. This was further investigated by measuring the influence of bromide on the value of  $T_a$  for tones due to increasing exposures. Plates exposed in the sensitometer or behind an intensity scale were developed with increasing quantities of bromide and the relative times of appearance observed. For this the following

FIG. 20.—*Effect of bromide on the "time of appearance."*



special apparatus was used. A clockwork motor drove a tape continuously beneath two pens, both recording lines upon it. Each pen was connected to the armature of a separate small electro-magnet in circuit with an accumulator. The current for one ran through a clock which made contact every second, thus marking off seconds on the tape; contact for the other could be made at the time of appearance of each tone. The plates were developed in a dish rocked before a lamp giving a fairly intense steady reddish light. The experiments were by no means easy to perform, and there were several failures.

The juxtaposition of the tones by the sensitometer increases the uncertainty as to the exact time of appearance, and it appears now that fewer tones spatially separated on the plate would give a better result. After interpreting and reducing the tapes, curves were constructed in which the values of  $T_a$  were plotted against the logarithm of the exposure. These are similar to the characteristic plate-curve, and show that in normal development the time of appearance is inversely proportional to the final density:—

TABLE 50.

No.	1.	2.	3.	4.	5.	6.	7.	8.	9.
Log E	3'31	3'01	2'72	2'42	2'14	1'80	1'575	1'36	1'00
$T_a$ in secs.	30'1	32'5	45'1	55'3	90'0	115'2	134'9	144'0	160'0
D ...	1'020	1'00	0'707	0'580	0'350	0'287	0'244	0'215	0'178
$T_a \times D$	30'4	32'5	31'9	32'0	31'4	33'1	33'0	30'9	27'8

The influence of bromide was tested from  $n/1000$  to  $n/125$ , the developer being  $n/25$  ferrous oxalate.

TABLE 51.

$T_a$  in seconds.

No.	Log E.	$n = 0.$	$n/1000.$	$n/500.$	$n/250.$	$n/125.$
1	3'80	12'8	21'6	26'5	31'5	37'9
2	3'46	14'0	22'3	28'8	32'5	39'3
3	3'30	14'7	23'6	30'0	36'5	42'9
4	3'13	17'9	27'8	30'5	41'5	52'4
5	2'79	22'0	30'0	34'5	47'0	60'8
6	2'41	24'8	32'6	39'7	62'0	74'0
7	2'06	27'6	40'2	50'8	79'6	84'2
8	1'72	37'0	57'6	68'7	90'0	107'6
9	1'34	45'0	70'0	79'8	110'3	—

From these numbers the retardation time was obtained, *i.e.*  $T_a$  for bromide —  $T_a$  for no bromide. Multiplying this value by the exposure logarithm, the following table was obtained:—

TABLE 52.

No.	Log E.	A = T <sub>r</sub> × log E.			
		n/1000.	n/500.	n/250.	n/125.
1	3·80	33·5	52·0	71·2	95·5
2	3·46	25·3	51·2	66·0	87·5
3	3·30	29·4	50·0	72·0	93·0
4	3·13	31·3	39·8	74·2	108·0
5	2·79	22·3	35·0	69·7	108·2
6	2·41	21·8	34·9	106·8	137·1
7	2·06	26·0	47·4	107·0	116·5
8	1·72	33·7	54·5	91·0	121·0
9	1·34	33·5	45·6	87·2	—
Mean	...	31·0	45·7	82·6	108·7

In spite of considerable fluctuations, probably not outside the experimental error, we have as a first approximation that the retardation is inversely as the logarithm of the exposure. It has been previously shown that for a single exposure the retardation is directly proportional to the logarithm of the bromide concentration. This was confirmed for the new series, the main deviations occurring with the lower exposures where the errors are greatest. In general, therefore, the retardation due to bromide may be expressed as—

$$T_r = T_a' - T_a = \frac{\phi([\text{Br})}{\phi'(E)}$$

and as a first approximation we find—

$$T_r = T_a' - T_a = \frac{c \log [\text{Br}]}{\log E}$$

where  $c$  is a constant, and  $T_a'$  and  $T_a$  the respective times of appearance in a bromided and non-bromided developer. The velocity formula might be written—

$$\log \frac{D_\infty}{D_\infty - D} = K(t - t_r) = K\left(t - \frac{c \log [\text{Br}]}{\log E}\right)$$

This explains the parallel shifting of the exposure curves, and

the "regression" of the inertia to its true value on infinite development, since  $t_r$  becomes increasingly less important as  $t$  increases. But as shown before, a better empirical correction for the velocity is included in the formula—

$$D = D_{\infty}(1 - e^{-Kt}) - \frac{K'[\text{Br}]}{t}$$

For  $t = \infty$  or  $[\text{Br} = 0]$ , this reduces to the normal formula—

$$\frac{1}{t} \log \frac{D_{\infty}}{D_{\infty} - D} = K$$

while for the retardation time  $t_r$ , since  $D = 0$ , we get—

$$D_{\infty}(1 - e^{-Kt_r}) = \frac{K'[\text{Br}]}{t_r}$$

whence—

$$t + K \log t = \frac{K'' \log [\text{Br}]}{\log D_{\infty}} = \frac{K'' \log [\text{Br}]}{\phi(E)}$$

a form not differing much from the former.

This equation,  $D = D_{\infty}(1 - e^{-Kt}) - \frac{K'[\text{Br}]}{t}$ , obtained from the data in Tables 46 and 47, expresses the fact that the velocity is retarded at the start by the reverse reaction, but that as metallic silver is deposited, the chemical reaction is accelerated, until ultimately the rate depends only on diffusion. Generally speaking, the problem is to "couple" the effects due to diffusion and chemical velocity. That the retarding effect is due to the free bromide ion appears probable from the following results. The plates were developed for 3.0 minutes at  $20^{\circ}$  in  $n/20$  ferrous oxalate, one with no bromide, the others in solutions  $n/100$  with respect to the bromine atom. It will be seen that the bromides of sodium, lithium, and ammonium give practically equal depressions, that due to potassium bromide is slightly less, whilst cadmium bromide at the same equivalent concentration gives a much lower depression. This slighter effect is no doubt due to its smaller ionization and its tendency to form complex ions such as  $\text{CdBr}_3'$ ,  $\text{CdBr}_4'$ .

TABLE 53.

No.	Log E.	D <sub>0</sub> .	Δ D for				
			KBr.	NaBr.	LiBr.	NH <sub>4</sub> Br.	1/2 Cd Br <sub>2</sub> .
1	1'00	0'020	0'020	0'019	0'020	0'020	0'020
2	1'36	0'080	0'065	0'080	0'080	0'072	0'045
3	1'575	0'175	0'135	0'145	0'130	0'124	0'146
4	1'80	0'326	0'216	0'280	0'290	0'282	0'178
5	2'14	0'520	0'282	0'290	0'295	0'286	0'180
6	2'42	0'722	0'302	0'294	0'310	0'290	0'183
7	2'72	0'930	0'312	0'320	0'318	0'325	0'194
8	3'01	1'099	0'266	0'312	0'320	0'321	0'187
9	3'30	1'312	0'280	0'300	0'300	0'297	0'182
Mean Δ D (for constant period) }			0'290	0'300	0'303	0'300	0'184

**The Nature of the Latent Image.**—The bearing of the foregoing investigation on this question will be discussed more fully in the final section. Meanwhile, it may be noted that both portions tend, on the whole, to exclude the view that the latent image consists of metallic silver. In the first place, oxidizing ferric-ferrous oxalate solutions which bleached negatives and would not develop, had no destructive effect on the latent image, the potential of which is, therefore, considerably different from metallic silver. Secondly, the initial induction rendered evident by bromide is hardly consistent with this view, which has, indeed, been generally abandoned since Luther's work.

**"Normal" and "Retarded" Development.**—The distinction has sometimes been somewhat vaguely made between "normal" and "retarded" development.<sup>1</sup> The results obtained here permit us to give some degree of precision to these terms. In *normal* development, the density-growth is conditioned by diffusion processes; the exposure only determines the number of grains available for development, and hence the density-ratios are constant. In *retarded* development the chemical

<sup>1</sup> J. Precht, *Zeit. wiss. Phot.*, i. 262.

velocity is comparable with, or less than, that of diffusion, so that not only the number but also the varying reactivity of the silver halide grains comes into play, resulting in different scales of gradation for different stages of development.

The complete effect of bromide on the exposure curve cannot be represented by any one simple expression over the whole range, the best approximation being that  $\Delta \log E$  is constant, that is, the curve is shifted parallel along the exposure axis. The bearing of the bromide results on the mechanism of light-action will be discussed later, but it will be seen that it brings into prominence the *reactivity* of the grains. Taking a chemical view of the latent image, this expresses the amount of the photo-product, the mass of which per grain continues to increase when the number of grains rendered developable has, in agreement with certain considerations regarding the absorption of light by the film, reached a maximum. It will be seen that the phenomena brought forward are in full agreement with the "silver germ" theory of development proposed by Ostwald and Abegg and modified by K. Schaum.<sup>1</sup> The main conclusion is the establishment of a criterion between diffusion and chemical action in heterogeneous reactions. If the concentration of the component present as solid phase can be altered, or if the reaction products be added, and either operation change the velocity, then this depends at least in part on the chemical reaction.

Retardation, with its characteristic regression of the inertia, may be brought about (*a*) by lowering the concentration of the silver ion, (*b*) by reducing the potential of the reducer. This second method will be dealt with under alkaline development. The concentration of the silver ion may be lowered by the addition of free halide ions in the manner dealt with, or by the formation of complex ions; this is dealt with in the next chapter.

<sup>1</sup> *Arch. wiss. Phot., loc. cit.*

## CHAPTER IV

### THE THEORY OF FIXATION AND THE ACTION OF COMPLEX SILVER IONS IN DEVELOPMENT

It appeared probable that if the rate of "fixation" could be measured, *i.e.* the rate at which the silver halides are dissolved by chemical solvents such as thiosulphate, useful data as to the parts played by diffusion and chemical action for a photographic reaction, independent of the peculiarities of development, such as the function of the latent image, might be obtained.

**Bibliography.**—No quantitative work appears to have been done on fixation. Some scattered observations on the nature of the process may be found in the following:—

Abney, Sir W., *Instruction in Photography*, 10th edit.

Eder, Dr. J. M., *Ausfuhr. Hdbuch.*, 2nd edit., III. 828 (1903).

E. Englisch, "Das Verhalten der Bromsilbergelatine im Grenzgebiet der Solarisation," *Zeit. wiss. Phot.*, I. 364-376.

A. & L. Lumière and E. Seyewetz, "Nature and Causes of Dichroic Fog," *Phot. Journ.*, 1903, 226.

T. Thorne Baker, "Simultaneous Development and Fixation," *Phot. Journ.*, 1904, I.

Further, on the general theory of reaction velocity in heterogeneous systems, see—

M. Wilderman, *Zeit. phys. Chem.*, 1899, 30. 341-382; *Phil. Mag.*, 1901, 50, 1902, 468.

W. Nernst, *Zeit. phys. Chem.*, 1904, 47. 52.

E. Brunner, *Zeit. phys. Chem.*, 1904, 47. 56-102.

Sand, *Roy. Soc. Proc.*, 1905, 74. 356.

G. Senter, *ibid.*, 1905, 74. 566.

**Experimental Method.**—It has been shown<sup>1</sup> that the quantity of silver haloid in the photographic film can be determined photometrically. But it is necessary to take precautions to avoid losing the "scattered" light.<sup>2</sup> This was accomplished by inserting milk-glass between the film and the light-source, so that a diffusing light-source was used. Further, when the haloids were measured, a narrow beam was employed, by means of the special screen and carriers.

That the scatter difficulty was overcome is evident from the following measurements :—

$D_A$  = density with milk-glass.

$D_B$  = density without milk-glass.

Distance of light-source.	$D_A$ .	$D_B$ .
4 cms.	1'120	1'250
6    "	1'130	1'300
10   "	1'105	1'421
12   "	1'141	1'443

Further, as the plates tended to darken somewhat on exposure, especially after treatment with thiosulphate, a yellow gelatoid filter was used to cut off the blue and violet. The first experiments, with sodium thiosulphate, were made by stirring in the thermostat, just as development took place. It seems preferable, however, to describe the second method first and then pass on to the effect of stirring. The solutions used were prepared from dinormal  $\text{Na}_2\text{S}_2\text{O}_3$ . In this method the plates were "fixed" in the Schulz cell of the spectrophotometer, readings being taken throughout the course of the

<sup>1</sup> *Roy. Soc. Proc.*, 1905, 74. 453.

<sup>2</sup> Abney, *Phil. Mag.*, 1875, V. 50; C. Jones, *Phot. Journ.*, 1898, 99.



reaction. The zero was fixed first with the cell (11 mm.) and solution. We have in all cases reduced the results to an original density of 1.00, although, as will be explained later, in view of the nature of the process, this does not make the absolute values strictly comparable.

If  $D_0$  be the original density, and  $D$  that at any time  $t$ , then  $D_0/D_0 - D/D_0 = (1 - D/D_0)$  gives the amount of halide dissolved, and this plotted against the time gives the velocity curve.

TABLE 54.

0.20 molar  $\text{Na}_2\text{SO}_3$ .  $D_0A = 1.30$ .  $D_0B = 1.18$ .

Time in minutes.	$(1 - D/D_0)_A$	$(1 - D/D_0)_B$
0.0	0.0	0.0
0.5	0.0	0.0
1.5	0.04	0.045
2.0	0.04	0.050
2.5	0.07	0.090
3.0	0.085	0.115
3.5	0.135	0.165
4.0	0.140	0.190
4.5	—	0.210
5.0	0.240	0.255
5.5	0.245	0.310
6.0	0.305	0.365
6.5	0.350	0.440
7.0	0.435	0.490
7.5	0.510	0.595
8.0	0.587	0.720
8.5	0.655	0.806
9.0	0.745	0.870
9.5	0.843	0.953
10.0	0.917	—
10.5	0.962	—
11.0	0.980	—

The difference in behaviour between plates A and B is not in the velocity as measured by  $-dD/dt$ , but simply in the total time required; this is due to the fact that A was denser than

B in the ratio of 1.30 to 1.18. The curves show that the velocity is the same.

TABLE 55.

0.10 molar  $\text{Na}_2\text{S}_2\text{O}_3$ .  $D_0 = 1.26$ .  $x = 1 - D/D_0$ .

Time in minutes.	$x_A$	$x_B$
0'0	0'0	0'0
2'0	0'0	0'0
4'0	0'025	—
5'0	0'046	0'048
6'0	0'063	—
7'0	0'089	0'115
8'0	0'105	—
9'0	0'133	0'146
10'0	0'188	0'174
11'0	0'213	0'233
12'0	0'257	0'262
13'0	0'295	0'303
14'0	0'366	0'370
15'0	0'423	0'423
16'0	0'494	0'479
17'0	0'570	0'573
18'0	0'657	0'690
19'0	0'734	—
20'0	0'811	0'776
21'0	0'870	0'845
22'0	0'922	0'930
23'0	0'958	0'978

A = no bromide. B =  $n/10$  KBr.

The two foregoing series show that  $n/10$  KBr has absolutely no influence on the velocity. As this result is fundamental to the theory of the reaction, it was repeated several times, and in no case was any decrease in the velocity observed.

TABLE 56.

0.05 molar  $\text{Na}_2\text{S}_2\text{O}_3$ .  $D_0 = 1.068$ .

Time in mins.	$x$ .	Time in mins.	$x$ .
0.0	0.0	30.0	0.414
5.0	0.0	31.0	0.456
8.0	0.035	32.0	0.487
10.0	0.045	33.0	0.509
16.0	0.124	34.0	0.553
19.0	0.164	35.0	0.586
20.0	0.187	36.0	0.643
21.0	0.203	37.0	0.667
22.0	0.215	38.0	0.714
23.0	0.252	39.0	0.747
24.0	0.275	40.0	0.775
25.0	0.295	41.0	0.847
26.0	0.310	42.0	0.857
27.0	0.315	43.0	0.902
28.0	0.370	44.0	0.942
29.0	0.385	45.0	0.958

TABLE 57.

0.04 molar  $\text{Na}_2\text{S}_2\text{O}_3$ .  $D_0 = 1.26$ .

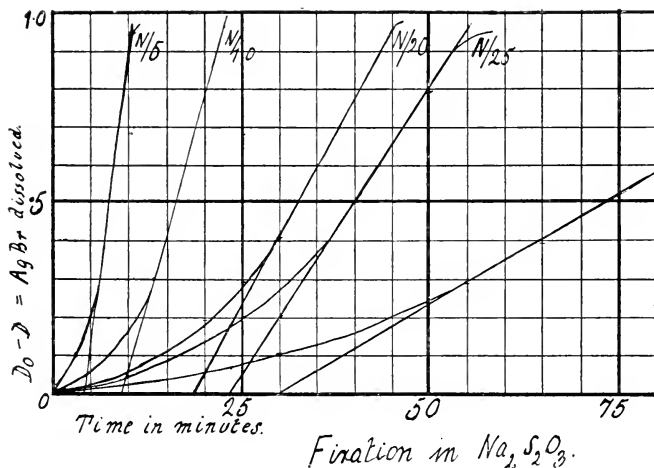
Time in mins.	$x$ .	Time in mins.	$x$ .
0.0	0.0	35.0	0.355
8.0	0.05	36.0	0.388
9.0	0.07	37.0	0.418
11.0	0.065	38.0	0.422
12.0	0.075	39.0	0.474
13.5	0.100	40.0	0.479
16.5	0.125	41.0	0.515
18.0	0.160	42.0	0.538
19.0	0.180	43.0	0.594
21.0	0.180	44.0	0.608
22.0	0.190	45.0	0.654
23.0	0.202	46.0	0.690
24.0	0.200	47.0	0.704
25.0	0.205	48.0	0.726
26.0	0.225	49.0	0.777
27.0	0.240	50.0	0.806
28.0	0.242	51.0	0.813
29.0	0.262	52.0	0.827
30.0	0.287	53.0	0.867
31.0	0.292	55.0	0.917
32.0	0.300	56.0	0.927
33.0	0.330	57.0	0.936
34.0	0.340	58.0	0.957

TABLE 58.

0.02 molar  $\text{Na}_2\text{S}_2\text{O}_3$ .  $D_0 = 1.094$ .

Time in mins.	$x$ .	Time in mins.	$x$ .
0.0	0.000	63.0	0.385
8.0	0.005	66.0	0.422
10.0	0.015	67.0	0.425
12.0	0.030	68.0	0.435
14.0	0.040	71.0	0.490
16.0	0.050	75.0	0.528
18.0	0.054	77.0	0.549
22.0	0.070	79.0	0.562
26.0	0.090	80.0	0.565
35.0	0.170	83.0	0.620
38.0	0.183	85.0	0.649
43.0	0.204	86.0	0.654
47.0	0.244	89.0	0.688
50.0	0.273	94.0	0.733
55.0	0.286	99.0	0.773
60.0	0.355		

FIG. 21.



The results for the various concentrations are given together as curves (Fig. 22). The form of the fixation-function under the given conditions is fairly obvious. If  $x$

be the amount of AgBr dissolved,  $dx/dt$  increases at first, and then becomes constant ; *i.e.*  $dx/dt = F$ , or, integrated—

$$x = Ft + B \text{ in steady state}$$

In the curves  $F = \tan \theta$ , and we get for the various concentrations—

TABLE 59.

Conc. of $\text{Na}_2\text{S}_2\text{O}_3$ .	F.	F/C.	B.	(B $\times$ C).
0.20 m.	7.32	36.6	4.0 mins.	0.80
0.10 "	3.54	35.4	9.0 "	0.90
0.05 "	1.81	36.2	18.0 "	0.90
0.04 "	1.50	37.5	24.0 "	0.96
0.02 "	0.60	30.0	30.0 "	0.60

Hence, the velocity of fixation is directly proportional to the concentration, the deviation of 0.02m being sufficiently accounted for by the fact that the concentration of the  $\text{Na}_2\text{S}_2\text{O}_3$  was not very great in this case compared with the AgBr dissolved. The cell only holds about 2 c.c., which for 0.02m contains only 0.006 gram  $\text{Na}_2\text{S}_2\text{O}_3$ .

These results with Wratten ordinary emulsion were compared with a Wratten speed plate in 0.2m  $\text{Na}_2\text{S}_2\text{O}_3$ .

TABLE 60.

0.2m  $\text{Na}_2\text{S}_2\text{O}_3$ . Speed plate.  $D_0 = 1.136$ .

Time in mins.	$x$ .	Time in mins.	$x$ .
0.0	0.0	19.0	0.342
6.0	0.05	20.5	0.402
8.0	0.08	21.0	0.433
9.5	0.127	22.0	0.468
10.0	0.130	23.0	0.508
11.0	0.137	24.0	0.548
12.5	0.172	25.0	0.619
13.0	0.180	26.0	0.700
14.0	0.196	27.0	0.754
15.5	0.232	28.0	0.819
16.0	0.270	29.0	0.908
17.0	0.279	30.0	0.930
18.0	0.327	—	—

With W.O. for comparison,  $dx/dt = F = 2.75$  Speed.  
7.35 Ordinary.

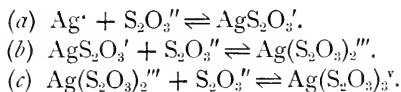
The greater rapidity of solution of the ordinary plate is probably due to its finer grain, and possibly also to its containing less silver iodide. A similar experiment was performed with a gelatino-chloride plate, in 0.10*m* Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. It will be seen that the action was extremely rapid.

TABLE 61.  
Chloride plate in 0.10*m* Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>.  $D_0 = 1.035$ .

Time in minutes.	$x$ .	$-dx/dt$ .
0.0	0.0	—
1.5	0.048	0.083
2.0	0.155	0.107
2.5	0.240	0.085
3.0	0.410	0.170
3.5	0.568	0.158
4.0	0.769	0.201
4.5	0.904	0.135

The action was much more rapid than with the bromide plate. Before proceeding further, we may consider the theory of the process.

**Theoretical.**—The action of so-called “fixing” agents is due to the formation of double salts, or according to the ionization theory, of complex ions. Thus we have for AgBr and Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> the following series :—



Now, for a given halide the efficiency of the fixing agent will depend upon the stability of the complex ion formed, *i.e.* the reciprocal value of its dissociation constant. This may be deduced in some cases from solubility determinations,<sup>1</sup> or from the E.M.F. of concentration cells in which the masses of the silver salt and solvent molecule are varied.<sup>2</sup> Thus the stability

<sup>1</sup> For ferrous oxalate, see *Trans. Chem. Soc.*, 1905, **87**. 189.

<sup>2</sup> G. Büdlander, *Chem. Centr.*, 1901, **ii**. 1109-1111.

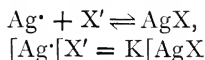
constant of the complex  $\text{Ag}(\text{S}_2\text{O}_3)'''$  is defined by the expression—

$$\frac{[\text{Ag}'] [\text{S}_2\text{O}_3'']^2}{[\text{Ag}(\text{S}_2\text{O}_3)''']} = K$$

The following data, taken from Böldlander,<sup>1</sup> give the stability constants of some complex silver ions, as also the concentration limit of the free anion :—

Formula of ion-complex.	Conc. limit of free anion.	K = stability constant.
$\text{Ag}(\text{S}_2\text{O}_3)_2'''$	below 0.1 <i>n</i>	$0.98 \times 10^{13}$
$\text{Ag}(\text{S}_2\text{O}_3)_3^v$	above 0.5 <i>n</i>	$3.45 \times 10^{13}$
$\text{Ag}(\text{CN})_2^I$	under 0.05 <i>n</i>	$0.11 \times 10^{22}$
$\text{Ag}_2\text{I}_4''$ to $\text{AgI}_4'''$	indefinite limits	$7.7 \times 10^{13}$
$\text{Ag}(\text{CNS})_2^I$	below 0.2 <i>n</i>	$6 \times 10^9$
$\text{Ag}(\text{CNS})_4'''$	above 0.3 <i>n</i>	$1.5 \times 10^{11}$

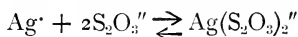
On the other hand, when the same solvent is used for different silver salts, the completeness of the reaction is determined by the solubility product of the silver salt.



and in the presence of solid salt,  $[\text{AgX}]$  is constant, so that  $[\text{Ag}][\text{X}'] = \text{constant}$ , the solubility product.

Hence the less soluble the given silver salt is in water, the higher must be the stability constant of the complex ion formed. To dissolve  $\text{Ag}_2\text{S}$ , the least soluble of silver compounds, KCN is required, other solvents being ineffectual.<sup>2</sup>

**The Influence of the Anion of the Solid Silver Salt.**—Obviously the concentration of the anion has a determining influence both on the velocity and the equilibrium conditions. Thus the velocity of the chemical reaction—



is given by—

$$-dx/dt = K[\text{Ag}'] [\text{S}_2\text{O}_3'']^2 - K'[\text{Ag}(\text{S}_2\text{O}_3)_2''']$$

<sup>1</sup> Ber., 1903, 36. 3933-3945.

<sup>2</sup> For the solubility products of silver salts, see Lucas, Zeit. anorg. Chem., 1904, 41. 193-215.

Considering the case when sufficient  $S_2O_3^{--}$  ion is present to neglect the reverse reaction, we get—

$$-dx/dt = K[Ag^+] = K/[X']$$

i.e. the velocity is inversely proportional to the concentration of the free anion.

Now, it has been shown that in the reaction with thio-sulphate and silver bromide, the velocity is unaffected by free bromide, even at  $n/10$  KBr. Hence it appears probable that under these conditions the measured rate of reaction depends solely on physical processes, the chemical velocity being great compared with these.

**Theory of the Process.**—The simplest explanation of the results obtained is that the rate measured is that of the penetration of the  $Na_2S_2O_3$  through the film, the chemical action being fast compared with this. Furthermore, the reaction differs markedly from development. In that  $dx/dt$  diminishes continuously from the start, whereas in fixation it increases up to a certain point and then remains constant. It appears to be somewhat similar to such actions as the rate of solution of a marble block by acids, and the reactions studied by Brunner (*loc. cit.*). For these the velocity is given by  $-dx/dt = \Delta/\delta(a-x)S$ , where  $S$  is the surface,  $\Delta$  the diffusivity of the reacting salt,  $\delta$  the diffusion layer,  $a$  the initial concentration, and  $x$  the equivalents of the solid dissolved at time  $t$ . In the case of the fixation,  $S$  would be the density of the AgBr per unit section, while if  $x$  be small compared with  $a$ , we have  $-dx/dt = \Delta/\delta a$ ,  $F = \text{constant}$ , as experimentally found. The increase of  $dD/dt$  in the first stage of fixation is probably due to the fact that the surface layers of films are somewhat poor in halide. This, which was also found in the microscopic examination, is probably in consequence of sedimentation, possibly assisted by surface-tension phenomena.

The great difference in the rate of fixation and of development is shown by the following. A plate soaked for five minutes in  $m/20$   $Na_2S_2O_3$  and then withdrawn showed no diminution of density in thirty minutes. Under similar circumstances development would be about  $1/3$  completed. This shows that for fixation the diffusion from the outer bulk of liquid



is much more important than in the case of development. It will be seen that the "mass-action" of the AgBr, which would lead to the velocity being proportional to the total quantity of AgBr in the film, does not come into play, except perhaps in the very last stages.

On the view developed above, it becomes possible to measure the influence of various substances on the diffusion of  $\text{Na}_2\text{S}_2\text{O}_3$  through the film. The following data as to the characters of the films are of interest:—

(a) Wratten speed: coarse grain, about 0.003 mm.; greater percentage of AgI; when heated in water, started to soften at  $42^\circ$ , melted at  $50^\circ$ .

(b) Wratten ordinary: grain about 0.0017 mm.; when heated in water, softened at  $50^\circ$ , melted about  $60^\circ$ .

(c) Chloride plate: AgCl; grain about 0.0007 mm.; melted at  $70^\circ$ .

It appears that it is not the films with the softest gelatine which fix most rapidly, but the rate depends rather on the composition and micro-character of the halide. This agrees with the following.

**Influence of Tanning.**—It has been previously found that "tanning" a film with formalin (40 per cent. formaldehyde) did not influence the development velocity. Similar results were obtained for fixation. A plate melting about  $40^\circ$  was soaked for fifteen minutes in 10 per cent. formaldehyde, which tanned it so as to become quite insoluble in boiling water. The rate of fixation of both in  $m/5$   $\text{Na}_2\text{S}_2\text{O}_3$  was measured, and the results are given in Table 46.

This shows that tanning or hardening the film with formalin has no influence on the velocity.

As a "tanning" action has been suggested in explanation of several phenomena in the exposure and development of gelatino-bromide plates, we made some further experiments on the velocity of diffusion in gelatine variously treated. But first a note as to the applications of this hypothesis. It was first suggested by Luther<sup>1</sup> that solarization or reversal was due to the halogen set free by exposure tanning the film, and so

<sup>1</sup> *Arch. wiss. Phot.*, 1900, ii.

preventing the diffusion of the developer. Englisch (*loc. cit.*) has similarly explained many phenomena in the region of over-exposure and solarization.

TABLE 62.  
(A) untanned; (B) tanned.

Time in mins.	$x_A$	$x_B$
0'0	0'0	0'0
6'0	0'05	0'055
8'0	0'08	0'120
9'5	0'127	0'140
12'0	0'168	0'176
13'5	0'190	0'207
14'0	0'196	0'213
15'5	0'232	0'250
17'0	0'279	0'275
18'0	0'327	0'320
19'0	0'342	0'332
20'0	0'402	0'424
21'0	0'433	0'440
22'0	0'468	0'473
23'0	0'508	0'540
24'0	0'548	0'562
25'0	0'619	0'620
26'0	0'700	0'685
27'0	0'754	0'755
28'0	0'819	0'814
29'0	0'908	0'886
30'0	0'930	0'943

Now, it may be noted that in ordinary colloids (gels) diffusion appears to take place as rapidly as in water,<sup>1</sup> while the saponification of methyl acetate is not affected by taking place in a jelly.<sup>2</sup> Hardening the colloid medium by raising its melting-point does not seem likely to alter the rate of diffusion in a gel, if we consider this as a two-phase system, a fluid enclosed in a capillary network.<sup>3</sup> The following

<sup>1</sup> Th. Graham, *Lieb. Annalen*, 121, 72; Voigtländer, *Zeit. phys. Chem.*, 1889, 3, 316.

<sup>2</sup> Reformatzky, *Zeit. phys. Chem.*, 1891, 7, 34.

<sup>3</sup> W. Nernst, *Theoret. Chem.*, 4th edit., 413; G. Quincke, *Ann. d. Phys.*, 4<sup>th</sup> Flge, II, 1100; Van Bemmeln, *Zeit. anorg. Chem.*, 1900-1, 23, 320.

experiments seem to confirm this. Solutions of acid and alkali in  $n/100$  strength were allowed to diffuse toward each other through cylinders of gelatine of equal height and strength of gelatine (5 per cent.), which had been variously treated. It was found that the time taken to meet was the same in plain gelatine, gelatine treated with weak bromide water and with 5 per cent. formaldehyde, although the M.P. was considerably raised. Similar results were obtained for the diffusion of hydroquinone and copper sulphate. On the other hand, the rate at which a dye was absorbed was much less in a hardened gelatine. *But in this case, generally an absorption of the dye to the colloid substance takes place.* A lessened absorption lowers the total diffusion in that the effective head or concentration gradient is less. It may be noted that this changed rate of dyeing is one of the chief arguments of those who favour "tanning" theories. As for the action of prolonged exposure, this was tested as follows: A portion of a Speed plate (*q.v.*) (*a*) which melted at  $42^{\circ}$  was exposed to sunlight for two hours (12 to 2 p.m.). Little or no difference was found in the melting-point between exposed and unexposed portions, while for the velocities of fixation in  $m/20$   $\text{Na}_2\text{S}_2\text{O}_3$  the values found for  $F = \frac{dD}{dt}$  in the steady state were—

*Unexposed*,  $F = 0.62$  (calc. 0.68).

*Exposed*,  $F = 0.65$ .

The calculated value was obtained from the data for  $m/5$   $\text{Na}_2\text{S}_2\text{O}_3$ , which with the Speed plate (*a*) gave (Table 44)  $F = 2.75$ . Assuming the velocity to be proportional to the concentration of the thiosulphate, this gives for  $m/20$   $\text{Na}_2\text{S}_2\text{O}_3$ ,  $F = 0.68$ . The result shows that the velocity of fixation is unchanged by prolonged exposure.

**Other Influences.**—It was found that the presence of both hydroxyl and hydrogen ions slightly increased the velocity of fixation, but not very markedly. Sodium thiosulphate in solution usually assumes a slight alkaline reaction; this is due, according to Thatcher,<sup>1</sup> not so much to hydrolysis as to aerial oxidation.

<sup>1</sup> *Zeit. physik. Chem.*, 1904, 47. 641.

**Influence of Stirring.**—In heterogeneous reactions in which diffusion determines the velocity, this is usually considerably increased by stirring. Experiments were made on fixation in the thermostat, the plates being measured dry in the special carriers. The procedure was as follows: The plate was dipped in water at the thermostat temperature for 2 to 3 minutes, rotated in the fixing agent for the determined time, then plunged into a solution of percarbonate of potash (supplied commercially as a "hypo-eliminator" under the names Hypax, Antithion, etc.), to stop the action, washed, dried, and measured. Considerable difficulty was experienced in getting concordant results, but on repeating and taking the means of several sets, a fair agreement was obtained, the results being then compared with those obtained without stirring. The temperature was  $20^{\circ}\text{C}$ ., while for the other method it was about  $18^{\circ}\text{C}$ ., the average room temperature. As the temperature coefficient is but slight, the comparison of the two sets is justified.

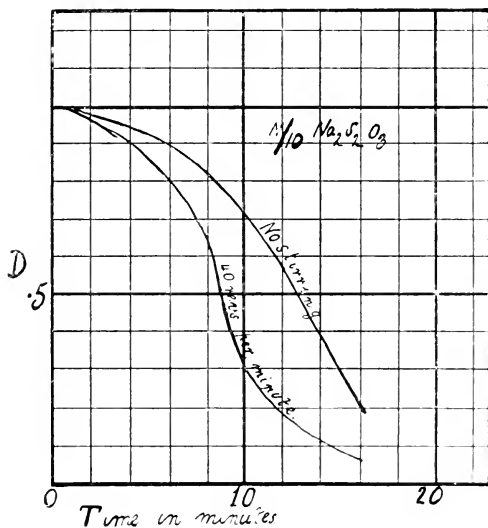
TABLE 63.

0.1*m*  $\text{Na}_2\text{S}_2\text{O}_3$ . (a) no stirring; (b) 40 revs. per minute.

Time in minutes.	$D_a$ .	$D_b$ .	$1/t_1 - t_2 \log D_1/D_2$ for <i>b</i> .
0'0	1'00	1'00	—
2'5	1'00	0'950	—
4'0	0'975	0'925	—
5'0	0'954	0'900	—
7'0	0'911	0'850	—
9'0	0'867	0'750	—
10'0	0'812	0'650	0'061
11'0	0'787	0'500	0'113
11'5	—	0'450	0'090
12'0	0'743	0'375	0'150
13'0	0'700	0'280	0'126
14'0	0'630	0'225	0'094
15'0	0'577	0'18	0'096
16'0	0'500	0'15	0'080
18'0	0'300	0'10	0'089
19'0	0'265	0'08	0'096
20'0	0'200	0'04	—

Mean  $K = 0.0995$ .

FIG. 22.



Obviously stirring not only increases the rate, but modifies the course of the reaction.

TABLE 64.

0.05*m*  $\text{Na}_2\text{S}_2\text{O}_3$ . (a) no stirring; (b) 40 revs. per minute.

Time in minutes.	$D_a$ .	$D_b$ .	$1/t_1 - t_2 \log D_1/D_2$ for <i>b</i> .
0.0	1.00	1.00	—
5.0	1.00	0.95	—
10.0	0.97	0.90	—
15.0	0.88	0.80	—
20.0	0.81	0.73	—
25.0	0.70	0.63	—
30.0	0.59	0.45	0.029
35.0	0.41	0.35	0.034
40.0	0.22	0.20	0.034
45.0	—	0.135	0.034

$$K = 0.033$$

FIG. 23.

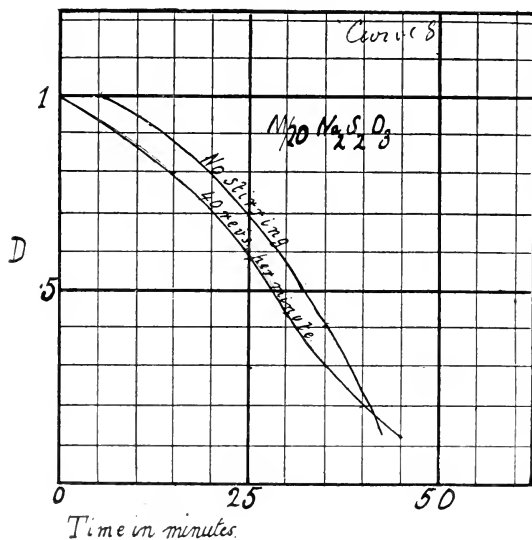


TABLE 65.

0.02*m* Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. (a) no stirring; (b) 40 revs. per minute.

Time in minutes.	D <sub>a</sub> .	D <sub>b</sub> .	1/t <sub>1</sub> - t <sub>2</sub> log D <sub>1</sub> /D <sub>2</sub> for b.
0.0	1.00	1.00	—
10.0	0.98	0.97	—
15.0	0.96	0.95	—
20.0	0.92	0.90	—
25.0	0.90	0.85	—
30.0	0.85	0.78	—
35.0	0.83	0.70	—
40.0	0.80	0.60	—
45.0	0.76	0.47	0.021
50.0	0.73	0.37	0.021
55.0	0.71	0.28	0.024
60.0	0.64	0.27	0.024

$$K = 0.023$$

The somewhat increased divergence is probably due to the

fact already noted, that with no stirring the volume of solution was small, only 2.0 c.c. compared with 100 c.c. with stirring. The general effect is the same.

Stirring greatly increases the velocity of the reaction. The induction period is less, and it appears that after some time the available surface is increased, the rate becoming proportional to the total mass or density of AgBr present. Under these conditions fixation follows the same function as development—

$$-dD/dt = KS = KD$$

or, integrating between  $t_1$  and  $t_2$ ,  $1/t_1 - t_2 \log D_1/D_2 = K$ , the relation to time becoming exponential instead of linear. This is even more marked with the fixing action of sodium sulphite on chloride plates, as the data now given show.

The relation of the velocity to the concentration was still the same—

Conc. of $\text{Na}_2\text{S}_2\text{O}_3$ .	0.1 <i>m</i> .	0.05 <i>m</i> .	0.02 <i>m</i> .
K	0.099	0.033	0.023

If we consider that stirring diminishes the length of the diffusion path *outside the film* (cf. Brunner, *loc. cit.*), so that a greater proportion of AgBr is included in the effective concentration gradient of the solvent, then with the much thinner gelatino-chloride plates we should expect the greater divergence produced by stirring.

**Fixation with  $\text{Na}_2\text{SO}_3$**  (sodium sulphite).—At moderate concentrations sulphite dissolves AgCl fairly rapidly, while at very great concentrations it has considerable solvent action on AgBr. We have not been able to find any data as to the formulæ and stability of the complex ions formed, but it is evident from the much slighter solubility of the silver salts in sulphite that they are much less stable than the corresponding thiosulphate complexes. Thus Valenta<sup>1</sup> gives the solubility of AgBr in 10 per cent.  $\text{Na}_2\text{S}_2\text{O}_3$  as 3.5 grams, while in 10 per cent.  $\text{Na}_2\text{SO}_3$  it is only 0.04 gram; AgCl at the same concentration, 4.4 and 0.44, whence the great influence of the solubility product of the silver salt is apparent.

The dissolution of AgBr by sulphite was too slow to be

<sup>1</sup> *Brit. Journ. Phot. Almanac*, 1904.

conveniently measured. In such cases as this it is evident that the diffusion of the solvent molecule is relatively fast, and the processes which determine the rate of reaction are the chemical action itself and the transference from the reaction layer of the products. Hence the theory of Nernst and Brunner requires some modification in such cases. Experimentally the reaction between sodium sulphite and gelatino-silver bromide was followed with and without stirring.

FIG. 24.

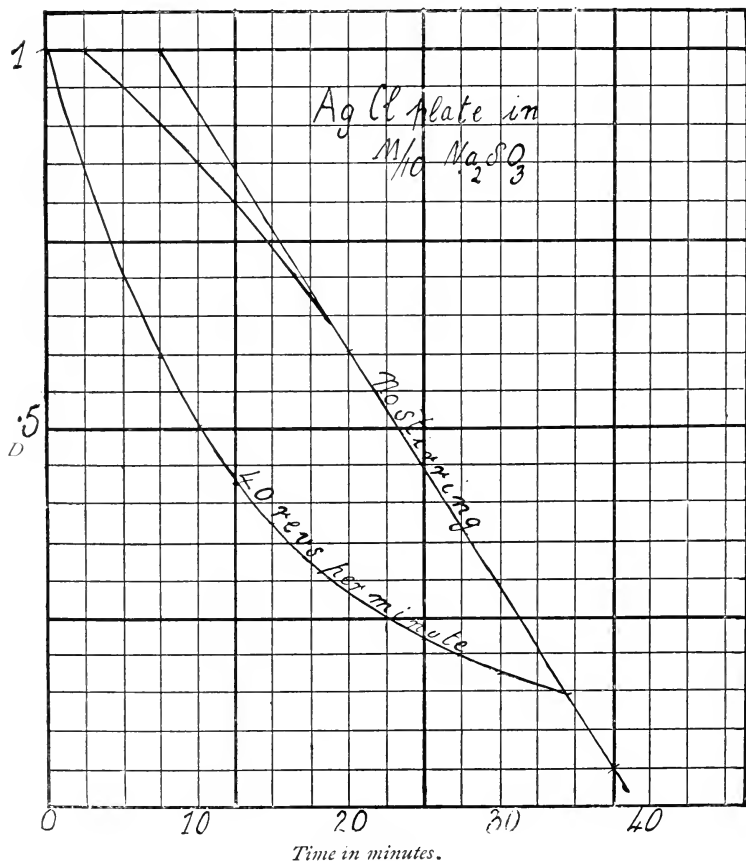




TABLE 66.

0.10*m* Na<sub>2</sub>SO<sub>3</sub> AgCl plate, no stirring.

Time in minutes.	D/D <sub>0</sub> .	1 - D/D <sub>0</sub> .	Time in minutes.	D/D <sub>0</sub> .	1 - D/D <sub>0</sub> .
0.0	1.00	0.0	24.5	0.507	0.493
3.5	1.00	0.0	26.0	0.457	0.543
4.0	0.974	0.026	27.0	0.398	0.602
5.0	0.945	0.055	28.0	0.388	0.612
6.0	0.915	0.085	29.0	0.356	0.644
8.5	0.890	0.110	30.0	0.320	0.680
9.5	0.865	0.135	31.0	0.280	0.720
12.0	0.810	0.190	31.5	0.252	0.748
14.0	0.786	0.214	32.5	0.223	0.777
15.0	0.743	0.257	33.5	0.201	0.799
16.0	0.685	0.305	34.0	0.194	0.806
17.0	0.712	0.288	35.0	0.157	0.843
18.0	0.698	0.302	36.0	0.146	0.854
19.0	0.683	0.317	37.0	0.091	0.909
20.0	0.631	0.369	37.5	0.102	0.898
21.0	0.593	0.407	38.0	0.085	0.915
22.0	0.572	0.428	39.0	0.057	0.943
23.0	0.547	0.453			

TABLE 67.

AgCl in 0.10*m* Na<sub>2</sub>SO<sub>3</sub>. 40 revs. per minute.

Time in minutes.	D/D <sub>0</sub> = <i>x</i> .	1/t - t <sub>2</sub> log D <sub>1</sub> /D <sub>2</sub> .
0.0	1.0	—
3.5	0.775	0.0314
5.0	0.70	0.0300
7.5	0.575	0.0325
10.0	0.50	0.0294
15.0	0.36	0.0291
20.0	0.28	0.0270
25.0	0.24	0.0240
30.0	0.20	0.0270
35.0	0.15	—

$$K = 0.029.$$

The action of stirring is therefore similar to that found with thiosulphate and AgBr.

The general conclusions from the investigation of fixation may be summarised as follows :—

(a) We can distinguish in the course of reactions in photo-films three main acts which take time :

( $\alpha$ ) The macro-diffusion through the film, a process of diffusion compounded with absorption : *invasion* or *penetration*.

( $\beta$ ) The micro-diffusion through the membrane of the grain ; very possibly this membrane is only semi-permeable with respect to certain ions : *permeation*.

( $\gamma$ ) The chemical action itself.

Development appears to depend chiefly on ( $\beta$ ) and ( $\gamma$ ), fixation on all three, but with normal solvents at sufficient concentration, chiefly on ( $\alpha$ ) and ( $\beta$ ).

(b) Tanning with formalin has no influence on fixation or development. Generally, the processes ( $\alpha$ ) and ( $\beta$ ) do not appear to be affected by tanning, but it is possible that chromium salts, especially when added during emulsification, have some effect. Prolonged exposure does not affect the rate of fixation.

**The Formation of Complex Ions and their Influence on Development.**—The addition to the developer of solvents for silver halides, such as sodium thiosulphate, thiocyanate, cyanide, thiosinamine, and so forth, has a pronounced influence on development. Before giving measurements to illustrate this effect, the actions likely to result may be considered.

While soluble bromides diminish the concentration of the silver ion, and at the same time lower the total solubility of the silver bromide, the formation of complex ions lowers the concentration of the silver ion, but increases the amount dissolved. We should expect from the behaviour of bromides that the development would be retarded, and the densities somewhat similarly depressed. This occurs, but with certain divergences and differences. The most important of these is the apparently radical difference between the action of  $\text{Na}_2\text{S}_2\text{O}_3$  with alkaline developers and with ferrous oxalate. With the former it produces in all cases a retardation and diminished density, but

with the latter an actual acceleration of development. In most cases the addition of silver solvents produces "fogs" of various types, while the plate-curve is generally more or less distorted. The following data illustrate these actions.

**Thiosulphate with Ferrous Oxalate.**—The accelerating action of thiosulphate has long been known and employed in practice.<sup>1</sup> It was studied both on the "time of appearance" and on the plate-curve. Abney attributed its effect to the decomposition of ferric oxalate, but this reaction, if occurring, is very slow, and the discussion of reversibility shows that it would in any case be probably inadequate.

TABLE 68.

$\text{N}_2\text{S}_2\text{O}_3$  in ferrous oxalate ;  $T_a$  = time of appearance.

Concentration.	$\text{Log } C \times 100.$	$T_a$ in seconds.	$V = 1/T_a.$
On	—	131.2	7.56
0.00005 <i>n</i>	0.699	131.5	7.61
0.00010	1.000	120.5	8.30
0.00015	1.175	108.0	9.25
0.00020	1.302	106.0	9.45
0.00025	1.397	103.5	9.75
0.00040	1.602	99.6	10.37
0.00050	1.699	74.0	13.50
0.0010	2.000	53.0	18.90
0.0015	2.175	43.7	22.9
0.0020	2.302	32.5	30.7
0.0025	2.397	27.6	35.6
0.0040	2.602	24.1	41.5
0.0050	2.699	19.6	51.0
0.0100	3.000	12.2	82.0

Evidently the acceleration is slight at first, and then increases more rapidly. It is not proportional either to the concentration or to the logarithm of this.

Both Abney and Lüppo-Kramer<sup>2</sup> state that "hypo" lowers the necessary exposure with ferrous oxalate. The influence on the characteristic curve was investigated, but the sensitometric bearing is noted later.

<sup>1</sup> Abney, *Instruct. in Phot.*, 9th edit., p. 181.

<sup>2</sup> *Wiss. Arb.*, Knapp, Halle.

TABLE 69.

3 to 10 minutes' development.

No $\text{Na}_2\text{S}_2\text{O}_3$ .		$n/1000 \text{ Na}_2\text{S}_2\text{O}_3$ .			
Log E.	$D_3$ .	$D_3$ .	$D_4$ .	$D_6$ .	$D_{10}$ .
1.36	0.244	0.409	0.497	0.531	0.547
1.575	0.382	0.703	0.761	0.806	1.023
1.80	0.604	1.001	1.105	1.272	1.410
2.14	0.865	1.180	1.503	1.797	2.080
2.42	1.137	1.402	1.860	2.295	2.673
2.72	1.387	1.613	2.139	2.558	3.219
3.01	1.640	1.937	2.296	2.920	—

At first the effect is chiefly noticeable for the lower tones, but as the time is increased it becomes relatively less for these and more marked in the higher densities. This divergence may be due in part to the somewhat heavy fog, both normal and dichroic, which tends to subtract relatively more from the lower densities; but it appears that two actions are at work—

- (a) A curtailment of the induction period, associated with the formation of *general*, *black* fog.
- (b) An intensification of the density formed by deposition of silver from the interaction of the complex silver ion with the developer: associated with the formation of *dichroic* fog, chiefly on the surface of the unexposed halide.

With greater concentrations of “hypo” and short development there is an apparent reversal brought about. This effect will be explained later.

Lüppo-Kramer (*loc. cit.*) considers that the “latent image” is favourably modified, as he states that a preliminary bath is as effective as when “hypo” is added to the developer. This was tested, the time of immersion being varied. Plates were soaked for  $T_i$ , rinsed by rotation one minute, then placed in the developer, and the “time of appearance” measured.

TABLE 70.

 $T_i$  = time of immersion ;  $T_a$  = time of appearance.

$T_i$ in seconds.	$T_a$ in seconds.	$T_a$ (mean value).
0	112'4, 112'4, 109'4	111'5
15	111'4, 109'8	110'6
30	105'0, 104'4, 105'2	104'9
45	99'0, 98'8, 98'4	98'7
60	99'0, 98'0, 98'2	98'4
120	99'6, 96'0, 100'0	98'5
300	93'0, 98'2, 95'4	95'5
600	96'2, 97'2	96'7

Practically the effect reached its limit in 45 seconds. As  $n/500$  hypo in the developer lowers  $T_a$  from 118'7 seconds to 29'2, and a preliminary bath at the same strength from 111'5 to 96 seconds, we may conclude that it is much more effective in the developer than as a preliminary bath. This suggests that the apparent preliminary effect may be due to some retention of hypo in the film.

Lumière and Seyewetz<sup>1</sup> have shown the tenacity with which this is retained. A parallel experiment with KBr showed that the film retained sufficient bromide after five minutes' washing to considerably influence the subsequent development. However, increased washing only slightly affected the result with thiosulphate. Experiments on the characteristic curve showed that it was impossible to completely wash out the hypo. Treatment with hypo destroyers (*vide* p. 126) lessened the effect partially, but not entirely. It appears probable that the thiosulphate is strongly absorbed by the silver bromide, possibly forming to some extent a solid solution, or traces of a solid double thiosulphate.

Before advancing any theory as to the effect, the action with alkaline developers may be described. With these there is no acceleration, but a retardation. On increasing very materially the hypo concentration, combined development and fixation becomes possible (Thorne Baker, *loc. cit.*). The retardation

<sup>1</sup> *Phot. Journ.*, 1902.

produced at  $n/100$  was slight, so that  $n/10$   $\text{Na}_2\text{S}_2\text{O}_3$  solutions were employed. The effect is somewhat similar to that with bromides, the value of  $\log i$  being altered, and a period of constant depression, which is, however, frequently masked by a distortion of the curve, hypo not acting as regularly as bromide.

TABLE 71.

*Hydroxylamine*, 4.0 minutes' development. (a)  $n/20$   $\text{NH}_2\text{OH}$  in  $n/20$   $\text{NaOH}$ ; (b) same with  $n/10$   $\text{Na}_2\text{S}_2\text{O}_3$ .

Log E.	$D_a$ .	$D_b$ .	$\Delta D$
1.00	0.107	0.065	0.052
1.36	0.260	0.152	0.108
1.575	0.461	0.376	0.185
1.80	0.801	0.582	0.219
2.14	1.123	0.870	0.253
2.42	1.430	1.225	0.215
2.72	1.725	1.473	0.252
3.01	2.036	1.721	0.315
3.30	2.312	1.880	0.432

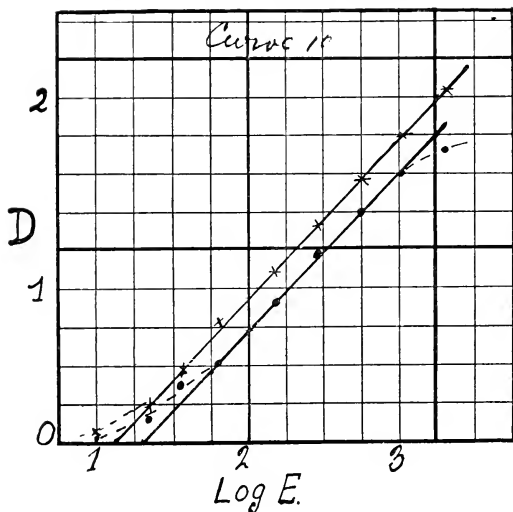
FIG. 25.—*Hypo in alkaline developer.*

TABLE 72.

*P*-amidophenol, 6.0 minutes' development. (a) *n*/10 phenol in *n*/10 NaOH; (b) same with *n*/10 Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>.

Log E.	D <sub>a</sub> .	D <sub>b</sub> .	ΔD.
1.00	0.156	0.142	0.014
1.36	0.523	0.405	0.118
1.575	0.964	0.736	0.228
1.80	1.591	1.324	0.267
2.14	2.193	1.790	0.423
2.42	2.430	1.978	0.452
2.72	2.701	2.300	0.401
3.01	3.052	2.620	0.432
3.30	3.463	2.819	0.644

**Theory as to the Action of Thiosulphates and other Silver Solvents in Development.**—The phenomena point to at least two, and probably three, actions in operation. The suggested factors are—

(a) Formation of a silver sulphide “germ.” This would occur probably only in an *acid* developer, where the decomposing influence of the hydrogen ions, forming sulphur, which, combining with silver by simultaneous reduction by the developer, would produce silver sulphide, more readily deposited on the exposed portions, but also in the unexposed, and hence accelerating both development and fogging. This question will be dealt with more fully under the “latent image,” but it may be noted in corroboration that polysulphides (liver of sulphur or ammonium sulphide) show the effect with ferrous oxalate at much lower concentrations than thiosulphate, it being visible at *n*/100,000.

In alkaline development the action suggested above would be nullified by the presence of OH' ions and SO<sub>3</sub>' ions, both tending to the stability of the thiosulphate.<sup>1</sup>

(b) The formation of complex silver ions would at first

<sup>1</sup> Cf. von Öttingen, *Zeit. phys. Chem.*, 30.

retard development by lowering the concentration of the silver ions. This effect was obtained with alkaline development.

(c) As the concentration of the solvent is increased, and thereby that of the complex silver ions, the velocity of the chemical reaction might be relatively increased instead of suffering a further diminution. F. Haber<sup>1</sup> has pointed out how inconceivably small is the active mass calculated for the free metallic cation in some complex solutions. Thus in a certain cyanide solution containing  $\text{Ag}(\text{CN})_3$  ions there are calculated to be only eight (8) silver ions per liter. Yet such solutions, in electrochemical and other reactions, behave as though the active mass were much greater. Ostwald suggests that the equilibrium constant (*vide* p. 121) is to be conceived as a time-ratio for the states of existence of the silver as cation and complex ion. This is rejected by Haber as postulating inconceivably great reaction velocities.<sup>2</sup> Haber concludes that the complex ion present in measurable quantities reacts directly. Whether this be so or the complexes decompose very rapidly, furnishing the silver ions sufficiently fast, it appears that a species of intensification or "physical" development takes place, which may increase the size of the grain and the density. Occurring also in the unexposed portions, this would, under certain conditions, give rise to dichroic fog as follows: In the absence of a germ to deposit silver upon, the solution of metallic silver would form a *colloidal* solution. Where this met a considerable concentration of an electrolyte it would be coagulated, and form a precipitate. This explains why dichroic fog in development is formed chiefly on the surface, and also why it is found mostly on the unexposed and underexposed portions, where "germs" for the deposition of metallic silver are wanting. All the researches of Lumière and Seyewetz<sup>3</sup> on the nature and formation of dichroic fog are in agreement with this view, which also explains why a reversal of the image is brought about by the prolonged development of under-

<sup>1</sup> *Zeit. Elektrochem.*, 1904, 10. 433.

<sup>2</sup> But see also Daneel, *Zeit. Elek. Chem.*, 1904, 601.

<sup>3</sup> *Phot. Journ.*, 1903, 43. 226.



exposures.<sup>1</sup> The overlapping or comparative predominance of one of these actions serves to explain the variety of the hypo effect under different development conditions and the distortion of the plate-curve. Furthermore, we have to take into account the comparatively slow penetration of the thio-sulphate, which, as shown in the preceding section, dissolves out the halide layer by layer. Hence normal development may be proceeding in the deeper layers while the modified action is at work in the upper ones. This is confirmed by the effect on plates exposed through the back; a greater distortion of the characteristic curve is produced, since the hypo has to penetrate deeper to reach the maximum reactive particles. As stated, the bending of the top part of the plate-curve sometimes amounts to reversal, which may, however, be removed by further development.

<sup>1</sup> Guébbard, *Bull. Soc. Trans. Phot.*, 1903, 44. 64.

## CHAPTER V

### ALKALINE DEVELOPMENT

IN modern photographic practice iron development is not much used, preference being given, for a variety of reasons, to the system of alkaline development introduced first according to Abney<sup>1</sup> by Major Russell in 1862. That there is no essential difference between the two methods will be abundantly evident in the sequel, but we may note a characteristic. The iron developers are used in slightly acid solution, the *amount* of acid having no effect on the strength of the solution or development, unless it be greatly increased,<sup>2</sup> but serving to prevent a formation of fog induced by alkali. On the other hand, the bodies used in alkaline development possess too feeble a developing power in acid solution for practical use, and the concentration of the alkali has a direct and controlling influence both on the composition of the solution and on the development. The following investigation may be conveniently dealt with in two parts.

PART I.—*On the Reactions between Hydroxylamine and Hydroperoxide respectively with Silver Salts, with some Notes on the Reactions of Organic Developers.*

While the stoichiometric relations between iron salts and silver halides are well known and simple, the same cannot be said of any other of the reducing agents, inorganic or organic, available as developers. So long as we are ignorant of the quantitative relation between reducer oxidised and silver halide reduced, as also of the former's oxidation product, the survey of

<sup>1</sup> *Instruct.*, 9th edit., p. 19.

<sup>2</sup> *Trans. Chem. Soc.*, 1905, **87**. 189.

development can only be tentative and approximate.<sup>1</sup> For organic developers we have the following methods and results:—

Reeb adds the reducing agent to a solution of silver oxide in alkaline sulphite; the silver precipitated is determined, and from this and the amount of reducer employed the “reducing power” of the developer is calculated. Somewhat similar was Hurter and Driffeld's determination of the reducing power of pyrogallol.<sup>2</sup> Using ammoniacal silver nitrate, they concluded that one molecule of pyrogallol reduced four molecules of AgBr. It may be objected to these methods that the reaction with solid silver halide may quite possibly take a different course, and in fact this will be subsequently shown to be the case.

Andresen<sup>3</sup> improved on the foregoing in this respect by adding the alkaline developer to excess of plain precipitated silver bromide, subsequently determining the metallic silver produced. Some of his results will be noted later, but it may be pointed out here that it is assumed without the proof of an independent estimation that the reducer is entirely oxidised.

Mention was made in the former thesis of the structural analogy that exists between organic reducers and the inorganic bodies  $\text{H}_2\text{O}_2$ ,  $\text{NH}_2\text{OH}$ , and  $\text{N}_2\text{H}_4$ , all of which can function as developers. On this account the reactions of the two former were quantitatively studied.

**Hydroxylamine and Silver Salts.**—The hydroxylamine was determined analytically by the method of Jones and Carpenter.<sup>4</sup> As finally evolved, the hydroxylamine solution is added slowly from a pipette to a well-stirred boiling copper solution, the most convenient being Soldaini's copper potassium carbonate.<sup>5</sup> The cuprous oxide precipitated was estimated by the method of Wood and Berry<sup>6</sup> and Sonntag,<sup>7</sup> used for sugars. It is collected on asbestos felt in a Gooch crucible, washed with boiling water, and transferred to a wide-mouthed bottle already

<sup>1</sup> Abegg, *Eder's Jahrbuch*, 1904, I; Sheppard and Mees, *Zeit. wiss. Phot.*, 1904, II. 10.

<sup>2</sup> *Phot. Journ.*, 1892, 22. 194.

<sup>3</sup> *Eder's Hdbuch.*, 1903, III. 312.

<sup>4</sup> *Trans. Chem. Soc.*, 1903, 83. 1394.

<sup>5</sup> *Gazz.*, 1876, 382.

<sup>6</sup> *Proc. Camb. Phil. Soc.*, 1902, 12. 2, 97.

<sup>7</sup> *Chem. Centr.*, 1903, I. 998.

filled with carbon dioxide. A solution of ferric salt, containing 35 grams ferric alum and 5 c.c. of strong sulphuric acid in 500 c.c., is added in sufficient quantity to dissolve the oxide, another portion being used to wash out any oxide adhering to the crucible. On shaking the bottle, the cuprous oxide is completely dissolved, and the ferrous salt is estimated with permanganate, when  $4\text{KMnO}_4$  correspond to  $10\text{NH}_2\text{OH}$ .

The hydroxylamine used throughout the subsequent work was prepared from commercial "pure" by recrystallisation from hot 98 per cent. alcohol containing a drop of platinic chloride, the crystals being dried *in vacuo* over sulphuric acid. Of a solution containing 0.9194 gram dissolved in 250 c.c., 20 c.c. were mixed with 20 c.c. *n*  $\text{AgNO}_3$ , and the excess of silver took 9.30 c.c. of 0.1*n*  $\text{KCNS}$ , factor 1.017. This gives  $\text{Cl} = 0.0375$ , theory 0.0376. Although this testified to the purity of the salt, at first too low results for the  $\text{NH}_2\text{OH}$  were obtained, the precautions as to mixing being stringently observed.

Conc. of $\text{NH}_2\text{OH}\cdot\text{HCl}$ .	No. of c.c. used.	c.c. of $\text{KMnO}_4$ .	Grams of $\text{KMnO}_4$ per c.c.	Grams of $\text{KMnO}_4$ per 1 gram-molecule $\text{NH}_2\text{OH}\cdot\text{HCl}$ .
0.9194 gram in 250 c.c.	20	22.5	0.00277	60.0
0.6542 gram in 200 c.c.	20	20.2	0.00277	61.4

Theory, 63.2

Other experiments gave 62.1 and 62.0 instead of 63.2. The discrepancies were traced to two causes, a reducing action on the permanganate by the asbestos used, and also loss of cuprous oxide or incidental oxidation of ferrous salt during the transference. With a purified asbestos and increased precautions satisfactory agreement was obtained. Thus 25 c.c. of a solution containing 0.6581 gram  $\text{NH}_2\text{OH}\cdot\text{HCl}$  in 200 c.c. were added to 50 c.c. of the copper solution, and the ferrous salt formed took 26.4 and 26.5 c.c. of the permanganate solution containing 0.0280 gram per c.c., which gives 63.0 and 63.1 grams of  $\text{KMnO}_4$  per gram-molecule of  $\text{NH}_2\text{OH}$ , instead of 63.2. From this and the chlorine determination the salt may be considered as pure.

**The Reaction between Alkaline Hydroxylamine and Silver Bromide.**—Ordinary precipitated silver bromide, whether exposed or not, is rapidly reduced by alkaline hydroxylamine. The reaction was carried out by red light, although this precaution is probably superfluous. The silver bromide was precipitated as a fine suspension by adding silver nitrate to some excess of potassium bromide solution, save when the reaction was carried out with no excess of bromide ions. In this case the silver bromide was precipitated with just over the theoretical amount of  $\text{HBr}$ , then washed and dried. Thus 5.0 c.c. of an  $\text{AgNO}_3$  solution, corresponding to 0.420 gram  $\text{Ag}$ , were taken, the  $\text{AgBr}$  after filtration on the pump placed in a stoppered bottle and shaken up with 50 c.c.  $\text{NH}_2\text{OH} \cdot \text{HCl}$  solution, containing 0.7020 gram, with 50 c.c.  $\text{NaOH}$ ; when the reaction, as indicated by the evolution of gas, had ceased, the solution was separated by levigation and neutralised with normal  $\text{H}_2\text{SO}_4$ . The residue was washed out with hot water, this added to the solution, and the latter made up to 250 c.c. This silver, after thorough washing, was dissolved in strong nitric acid, made up to a definite volume and titrated with decinormal  $\text{KCNS}$ . It was found that 0.198 gram of  $\text{NH}_2\text{OH} \cdot \text{HCl}$  disappeared, and 0.2956 gram  $\text{Ag}$  was produced, *i.e.* 104.2 grams  $\text{Ag}$  per gram-molecule of  $\text{NH}_2\text{OH}$ . Again, 50 c.c. of a solution, containing 0.3510 gram  $\text{NH}_2\text{OH} \cdot \text{HCl}$ , were added to 50 c.c.  $\text{AgNO}_3$  in 10 c.c.  $\text{KBr}$ . The solution, after reaction, was made up to 250 c.c., the silver to 150 c.c. Of the former, 50 c.c. were added to 25 c.c. of copper solution, and required 4.8 c.c.  $\text{KMnO}_4$ . Hence  $\text{NH}_2\text{OH} \cdot \text{HCl}$  left is 0.060 gram, while that used up is 0.291 gram. Of the silver solution, 25 c.c. took 8.0, 8.1, 8.1, mean = 8.07 c.c. of 0.1017  $\text{N}$   $\text{KCNS}$ ; hence in 150 c.c. there were 0.532 gram  $\text{Ag}$ . Thus 0.291 gram  $\text{NH}_2\text{OH} \cdot \text{HCl}$  disappeared for 0.532 gram  $\text{Ag}$  produced, or 127 grams  $\text{Ag}$  per gram-molecule of  $\text{NH}_2\text{OH} \cdot \text{HCl}$ . Before giving the tabulated results, a note on the sources of error is desirable. In addition to ordinary analytical error (the precautions in the estimation of hydroxylamine have been noted already), one likely cause of error is the spontaneous decomposition of alkaline hydroxylamine

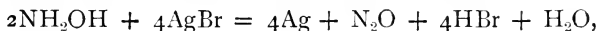
solutions. Berthelot<sup>1</sup> has shown that alkaline hydroxylamine solutions slowly decompose as follows:  $3\text{NH}_3\text{O} = \text{NH}_3 + \text{N}_2 + 3\text{H}_2\text{O}$ . Tanatar<sup>2</sup> has confirmed this, and also shown that the following decomposition occurs to some extent:  $4\text{NH}_3\text{O} = 2\text{NH}_3 + \text{N}_2\text{O} + 3\text{H}_2\text{O}$ . As this process is catalysed by finely divided silver, it was necessary to determine its extent for the time and under the conditions of the experiments. About 0.5 gram of silver obtained in an experiment was mixed with 50 c.c. of 0.1*N*  $\text{NH}_2\text{OH}.\text{HCl}$  and 25 c.c. of *n*  $\text{NaOH}$ , and left for an hour with frequent shakings at the room temperature of 18° C. On determining the  $\text{NH}_2\text{OH}$ , the discrepancy was less than  $\frac{1}{2}$  per cent. Another experiment, with more alkali and at twice the volume, gave a similar result, although in this case the mixture was left for three hours. Hence the error from this source appears to be negligible. Acid solutions of hydroxylamine may be preserved unchanged over long periods at ordinary temperatures, but appear to suffer some decomposition or boiling. Tabulating all results:—

Concentration of $\text{NH}_2\text{OH}.\text{HCl}$ .	Concentration of alkali.	Relative amounts of $\text{AgBr}$ and $\text{Br}'$ .	Grams $\text{Ag}$ per gram-molecule of $\text{NH}_2\text{OH}$ .
0.7020 gram in 100 c.c. = 0.10 <i>N</i> .	25 c.c. <i>n</i> $\text{NaOH}$ 0.40 <i>N</i> .	5 c.c. <i>n</i> $\text{AgNO}_3$ with 80 c.c. <i>n</i> $\text{KBr}$ .	127
0.7020 gram in 100 c.c. = 0.10 <i>N</i> .	50 c.c. <i>n</i> $\text{NaOH}$ 0.80 <i>N</i> .	3.9 c.c. <i>n</i> $\text{AgNO}_3$ ppd. with $\text{HBr}$ . No $\text{Br}'$ .	104.2
0.7028 gram in 100 c.c. = 0.1 <i>N</i> .	0.20 <i>N</i> .	3.9 c.c. <i>n</i> $\text{AgNO}_3$ with 5 c.c. <i>n</i> $\text{KBr}$ .	110.0
0.7028 gram in 100 c.c. = 0.1 <i>N</i> .	0.20 <i>N</i> .	5 c.c. <i>n</i> $\text{KBr}$ . 3.9 c.c. <i>n</i> $\text{AgNO}_3$ .	109.2
0.7028 gram in 100 c.c. = 0.1 <i>N</i> .	0.20 <i>N</i> .	5.0 c.c. <i>n</i> $\text{KBr}$ . 2.9 <i>n</i> $\text{AgNO}_3$ .	109.1
0.3503 gram in 200 c.c. = 0.025 <i>N</i> .	0.05 <i>N</i> .	2.0 <i>n</i> $\text{AgNO}_3$ . 3.0 c.c. <i>n</i> $\text{KBr}$ .	105.8

<sup>1</sup> *Ann. Chim. Phys.* [5], **10**, 433, 1877, and *ibid.* [6], **21**, 384, 1890.

<sup>2</sup> *Zeit. phys. Chem.*, 1902, **40**, 475.

The theory for the reaction  $2\text{NH}_2\text{OH} + 2\text{AgBr} = 2\text{Ag} + \text{N}_2 + 2\text{HBr} + 2\text{H}_2\text{O}$  would give 108 grams of Ag per gram-molecule of  $\text{NH}_2\text{OH}$ . It appears from these results that this reaction is nearly approached until the dilution of the  $\text{NH}_2\text{OH}$  becomes very considerable. In the experiment giving 127 grams Ag, the final concentration of the  $\text{NH}_2\text{OH}$  was only  $n/80$ . It seemed likely that at great dilution of the hydroxylamine the reaction would proceed according to the equation—



which would be similar to its behaviour with copper salts.<sup>1</sup> To test this, hydroxylamine solution was added to hot, well-stirred ammoniacal silver nitrate, the addition being made slowly from a pipette. The silver formed was estimated, the filtrate, when tested, showing no hydroxylamine. It was found that 0.0438 gram  $\text{NH}_2\text{OH} \cdot \text{HCl}$  had produced 0.1300 gram Ag, hence 206 grams Ag per gram-molecule  $\text{NH}_2\text{OH}$ . It appears that under these conditions the reaction  $2\text{NH}_2\text{OH} + 2\text{Ag}_2\text{O}$ , which would give 216 grams Ag, is approached. Further, it is evident that the addition of the reducer to ammoniacal silver nitrate may lead to a different reaction from that with silver bromide, and that it is not permissible to deduce the reducing power from this.

**Reaction of Hydroxylamine with Silver Oxide in Sulphite Solution.**—A preliminary experiment in which the hydroxylamine was added slowly to a heated solution of silver oxide in sodium sulphite solution gave 503 grams Ag per gram-molecule  $\text{NH}_2\text{OH}$ . This was found to be due to the instability of the solution at the higher temperature, the sulphite itself then taking part in the reaction. Below  $30^\circ$  it was found that silver sulphite solutions were fairly stable in the presence of finely divided silver, so the reaction was carried out in the cold. To 10 c.c.  $n$   $\text{AgNO}_3$  in 50 c.c. of saturated sodium sulphite, 25 c.c. of a 0.05  $n$   $\text{NH}_2\text{OH}$  solution were added. The reaction was slow in starting, but was accelerated by the addition of a trace of reduced silver, and caustic soda in the proportion of 3 mols.  $\text{NaOH}$  to 1 mol.  $\text{NaOH}$ . The precipitate was filtered off,

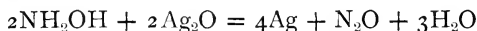
<sup>1</sup> Jones and Carpenter, *loc. cit.*

treated with HCl, washed, and, after dissolution in nitric acid, titrated with 0·1*N* KCNS.

(a) 0·3515 gram  $\text{NH}_2\text{OH} \cdot \text{HCl}$  gave 0·296 gram Ag, *i.e.* 188 grams Ag per gram-molecule  $\text{NH}_2\text{OH}$ .

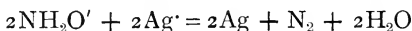
(b) 0·702 gram  $\text{NH}_2\text{OH} \cdot \text{HCl}$  gave 0·1795 gram Ag, *i.e.* 178 grams Ag per gram-molecule  $\text{NH}_2\text{OH}$ .

These low values were possibly due to the dilution of the  $\text{NH}_2\text{OH}$  not being satisfactorily maintained, owing to the low velocity of the reaction. An experiment was therefore made in which the silver sulphite solution was mechanically stirred, the hydroxylamine being added in drops at such a rate that the complete reaction took four hours. In this case 0·7020 gram  $\text{NH}_2\text{OH} \cdot \text{HCl}$  gave 0·2140 gram Ag, *i.e.* 212 grams Ag per gram-molecule of  $\text{NH}_2\text{OH}$ ; hence a better approximation to the reaction—



It appears from these results that Reeb's method for estimating the reducing power of developers is not reliable.

**The Nature of the Reaction between Hydroxylamine and Silver Salts.**—The reducing action of hydroxylamine, when set free from its salts, is greatly intensified by alkali. This is due to its being an amphoteric electrolyte, forming both hydrogen and hydroxyl ions,<sup>1</sup> hence acting as a base in the presence of acids, its salts being considerably hydrolysed,<sup>2</sup> while with strong bases it acts as a very weak acid. The two stages in which the oxidation of hydroxylamine may take place can be considered as arising from its function as a dibasic acid. Thus at moderate dilutions we have from the equilibrium  $\text{NH}_2\text{OH} + \text{NaOH} \rightleftharpoons \text{NH}_2\text{ONa} + \text{H}_2\text{O}$  the ion  $\text{NH}_2\text{O}'$ , which reacts with silver ions according to the equation—



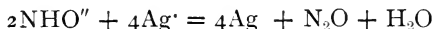
At greater dilutions the ionisation of the second hydrogen atom becomes appreciable, and from the equilibrium

<sup>1</sup> Winkelblech, *Zeit. phys. Chem.*, 1901, **36**, 550; J. Walker, *Roy. Soc. Proc.*, 1904, **73**, 155.

<sup>2</sup> The hydrochloride, etc., may be titrated with caustic alkalis, using methyl orange or phenolphthalein.



$\text{NH}_2\text{ONa} + \text{NaOH} \rightleftharpoons \text{NHONa}_2 + \text{H}_2\text{O}$  we have the ion  $\text{NHO}''$ , reacting according to the equation—



The coupling of the discharged ions  $\text{NH}_2\text{O}$  and  $\text{NHO}$  in the manner condensed above appears to offer a satisfactory explanation of the reactions of hydroxylamine with copper and silver salts, its behaviour being the same with both.

**The Effect of Gelatine.**—There is no reason to believe that the silver bromide in a gelatine emulsion reacts differently with a developer from ordinary precipitated silver bromide. However, to control the more easily accomplished estimations described in the foregoing, an attempt was made with silver bromide emulsion stripped from a plate. But this failed, as with the massed emulsion the reduction was too uneven and too slight. A more successful result was obtained as follows: Several  $\frac{1}{4}$  plates were given a full exposure and then developed to a high density in 100 c.c. of alkaline hydroxylamine. Of this solution 50 c.c. were removed and the hydroxylamine unoxidised was determined. The density of the plates was measured photometrically, and the silver estimated in a manner described previously.<sup>1</sup> The results were:—

Area of plate in C.M.S. <sup>2</sup>	Density, D (mean).	Silver in grams.	$\text{NH}_2\text{OH}$ } HCl } used up.	Ag per gram-mol. $\text{NH}_2\text{OH}$ .	P, <i>i.e.</i> Ag in grams per 100 C.M.S. <sup>2</sup> for D = 1.00.
5 × 87.2	3.01	0.139	0.0935	103.2	0.0103
5 × 87.2	3.21	0.145	0.0972	104.0	0.0104

This shows that in the development of silver bromide plates by hydroxylamine, 1 mol.  $\text{NH}_2\text{OH}$  reduces 1 mol.  $\text{AgBr}$ , and also that the “photometric constant,” or covering power of the silver reduced, is the same as for ferrous oxalate, which gave  $P = 0.01031$ .

### The Reaction between Hydrogen Peroxide in Alkaline

<sup>1</sup> *Roy. Soc. Proc.*, 1905, **74**, 451; also Chap. II., p. 40.

**Solution and Silver Bromide.**—Of the various methods proposed or in use for the determination of peroxide, the simplest and most convenient for this work was that by titration with permanganate in acid solution. The discrepancies occurring when sulphuric acid is used have been shown by Ramsay to be due to the formation of persulphuric acid, only being manifest when the peroxide is allowed time to react with the acid. The trouble may be completely avoided by using acetic acid, and this modification was adopted except in certain cases where the presence of a large quantity of alkali acetate so weakened the free acetic acid that it was unable to retain the manganese sesquioxide in solution. Preliminary experiments showed that it was desirable to add a little manganese sulphate to curtail the induction period of the reaction, and also that the glacial acetic first used contained an impurity which reduced permanganate. Some fresh glacial acetic was obtained and purified by redistillation over a little solid  $\text{KMnO}_4$ . Briefly summarised, the results for the original peroxide solution used were:—by titration with  $0.1N$   $\text{KMnO}_4$  in acetic acid solution,  $0.0344$  gram per c.c., added to  $0.1N$   $\text{KMnO}_4$  with sulphuric acid,  $0.0347$  gram, and with  $0.01N$   $\text{KMnO}_4$  in acetic acid,  $0.0342$  gram, of  $\text{H}_2\text{O}_2$  per c.c.

Since the time of Thénard,<sup>1</sup> the reactions between peroxide and silver compounds have been extensively investigated, but with somewhat confused and even contradictory results. The question as to the nature of the reaction is immensely complicated by the spontaneous decomposition of peroxide into water and oxygen, a process which is catalysed by a very large number of substances,<sup>2</sup> and in especial by finely divided and colloidal metals. Hence the metallic silver formed by the direct reduction of the silver halide is liable to assist a further decomposition, falsifying the relation obtained between the peroxide decomposed and the silver reduced. To allow for this as far as possible, an exactly similar solution of peroxide to that reacting with the silver bromide was identically treated for the same time with a quantity of reduced silver about half that

<sup>1</sup> *Ann. Chim. Phys.*, 1818, 9, 314.

<sup>2</sup> G. Bredig, *Anorg. Fermente*, Leipzig, 1901.

produced in the reaction, and the peroxide determined at the end. The results are expressed in the form of a "silver correction."

(a) To 5.0 c.c. of a solution containing 0.344 gram  $\text{H}_2\text{O}_2$  per c.c., diluted with 200 c.c.  $\text{NaOH}$ , a mixture of 2 c.c.  $n$   $\text{AgNO}_3$  with 2 c.c.  $n$   $\text{KBr}$  and 20 c.c. water was added. At the end of the reaction, which was comparatively slow, the solution was acidified with acetic acid, and after separation from the solid, made up to 250 c.c. Then 0.218 gram  $\text{H}_2\text{O}_2$  produced 0.550 gram  $\text{Ag}$ , or 86 grams  $\text{Ag}$  per gram-molecule of  $\text{H}_2\text{O}_2$ . The "silver correction" was equivalent to 151 grams  $\text{Ag}$ , whence we have 97 grams  $\text{Ag}$  per mol. of  $\text{H}_2\text{O}_2$ .

(b) The time of the reaction was shortened by using more silver bromide and shaking more frequently. For 0.1485 gram  $\text{H}_2\text{O}_2$  there was obtained 0.4126 gram  $\text{Ag}$ . This gives 94.5 grams  $\text{Ag}$  per mol. of  $\text{H}_2\text{O}_2$ , or, with the "silver correction" of 9.4 grams, 103.9 grams  $\text{Ag}$  per mol. of  $\text{H}_2\text{O}_2$ .

(c) In this 0.162 gram  $\text{H}_2\text{O}_2$  produced 0.4830 gram  $\text{Ag}$ , *i.e.* 101.2 grams  $\text{Ag}$  per mol. of  $\text{H}_2\text{O}_2$ . With the silver correction of 9.4 grams this makes 110.6 grams  $\text{Ag}$  per mol. of  $\text{H}_2\text{O}_2$ .

These results are sufficiently near the value 108 grams  $\text{Ag}$  to indicate that equimolecular quantities of silver bromide and peroxide react, but it remains to decide what the complete reaction equation is.

In these experiments the concentration of the peroxide was about 0.10*n* to 0.2*n*, the ratio of alkali being about 4 to 1 per gram-molecule. Hydrogen peroxide in solution acts as a weak acid, forming with strong bases salts which are considerably hydrolysed.<sup>1</sup> Considering the univalent ion  $\text{O}_2\text{H}'$ , formed according to the equilibrium  $\text{H.O}_2\text{H} + \text{NaOH} \rightleftharpoons \text{NaO}_2\text{H} + \text{H}_2\text{O}$ , the interaction with silver ions would be  $\text{O}_2\text{H}' + \text{Ag}^+ = \text{Ag} + \text{O}_2\text{H} -$ ; the complexes  $-\text{O}_2\text{H}$  coupling according to the scheme  $-\text{O}_2\text{H} + -\text{O}_2\text{H} = 2\text{O}_2 + \text{H}_2$ , we have condensed  $2\text{Ag}^+ + 2\text{O}_2\text{H}' = 2\text{Ag} + 2\text{O}_2 + \text{H}_2$ , *i.e.* hydrogen should be formed, in the proportion of one volume to two of oxygen. To test this the gases evolved from silver bromide in suspension added to alkaline peroxide were collected and analysed.

<sup>1</sup> Calvert, *Zeit. phys. Chem.*, 1901, **38**, 513.

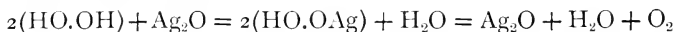
Quantities of hydrogen varying from 2 per cent. to 5 per cent., the remainder being oxygen, were obtained, showing at least that hydrogen is formed; but probably under the conditions of the experiment the proportion was masked by the oxygen from the catalytic decomposition and from the reaction  $\text{O}_2'' + 2\text{Ag}^* = \text{O}_2 + 2\text{Ag}$  (compare Hydroxylamine).

The interaction of hydroperoxide and silver oxide has been investigated in recent years by Berthelot and others.

Berthelot<sup>1</sup> considers that a peroxide of silver,  $\text{Ag}_2\text{O}_2$ , is formed, part of which decomposes into silver and oxygen, part into silver oxide and oxygen, while yet a third part combines with the silver oxide so produced to form an intermediary oxide,  $\text{Ag}_4\text{O}_3$ , which latter again decomposes to silver oxide and oxygen.

Baeyer and Villiger<sup>2</sup> confirm Thénard's statement that a mixture of hydroperoxide and silver oxide always evolves more oxygen than would be liberated by a catalytic decomposition of the peroxide. As the precipitate left evolves no further gas on treatment with dilute sulphuric acid, they cannot agree with the formation of the higher oxide  $\text{Ag}_4\text{O}_3$ . They consider that hydroperoxide and silver oxide react according to the equation  $\text{H}_2\text{O}_2 + \text{Ag}_2\text{O} = 2\text{Ag} + \text{O}_2 + \text{H}_2\text{O}$ , but subsequently a portion of the peroxide is catalytically decomposed by the finely divided silver produced. They find no experimental evidence for the existence of a higher oxide of silver.

E. Mulder<sup>3</sup> has treated weighed quantities of silver oxide, silver peroxide (?), carbonate, and nitrate with aqueous  $\text{H}_2\text{O}_2$ , evaporated to dryness in a desiccator, and determined the change of weight, if any. He recovered almost quantitatively all the substances except the carbonate, which was partially reduced to oxide. He suggests as typical of the changes involved the equation—



Loewenhardt and Kastle<sup>4</sup> consider that the so-called reductions with peroxide are oxidations in an initial stage,

<sup>1</sup> *Compt. Rend.*, 1901, **132**. 897.

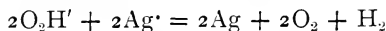
<sup>2</sup> *Ber.*, 1901, **34**. 749.

<sup>3</sup> *Rec. Chim. Trav.*, 1903, **22**. 388.

<sup>4</sup> *Amer. Chem. J.*, 1903, **29**. 397; and *ibid.*, 1903, **29**. 563.

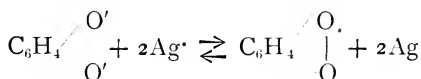
*i.e.* complex addition products are formed which then break down.

The views of these experimenters offer no explanation of the influence of alkalis in reduction with hydroperoxide. The experiments with alkaline peroxide acting on suspended silver bromide point, as shown, to the reaction—



the silver reduced then catalytically assisting a further decomposition of  $\text{H}_2\text{O}_2$ . This agrees rather with Bayer and Villiger's conception of the process, while all the work at present on the molecular condition in solution shows that  $\text{H}_2\text{O}_2$  functions as a weak acid, forming first the univalent ion  $\text{O}_2\text{H}'$ ,<sup>1</sup> and probably at greater dilution the divalent ion  $\text{O}_2''$ .

**On the Reactions of Hydroquinone, p-Amido-phenol, and other Organic Reducers with Silver Salts.**—All organic reducing agents available as developers are characterised by the following constitution. They are substituted aromatic derivatives containing at least two of the groups  $-\text{NH}_2$ ,  $-\text{OH}$ , or  $-\text{NH.X}$  (X being a substituted radical) in the ortho- or para- position, the meta-bodies not functioning as developers.<sup>2</sup> In investigating their actions with silver halides, great difficulty is experienced owing to their rapid autoxidation and other side reactions. No reliable method has yet been evolved for estimating these bodies in the presence of sulphites and alkalis, as they occur in developing solutions. Andresen states that according to his method hydroquinone reduces two molecules of silver bromide, but in the presence of sulphite, four. We have dealt with the chemistry of the hydroquinone developer elsewhere,<sup>3</sup> but the essential facts are as follows. There seems no reason to doubt that the primary oxidation of quinol in alkaline solution leads to the formation of quinone—



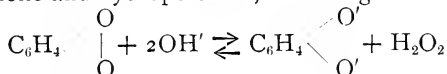
This equation has been written as reversible, since a solution

<sup>1</sup> Carrara and Brighenti, *Gazz.*, 1903, **33**, 362.

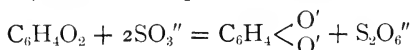
<sup>2</sup> *Eder's Jahrbuch*, 1899, 140-147.

<sup>3</sup> *Zeit. wiss. Phot.*, 1904, **II**, 5-11.

of quinone and potassium bromide bleaches a negative, converting the silver to silver bromide. But the addition of quinone has no retarding effect on development, and for the following reasons. Quinone reacts with alkalis, or hydroxyl ions, forming hydroquinone and hydroperoxide, according to the equation—



but in the presence of atmospheric oxygen more complicated bodies, together with tarry products, are formed which obscure the above reaction. The addition of KOH solution to a saturated quinone solution turns it red-brown, removes the quinone smell, while the solution possesses developing properties. To obtain a more controllable reaction, less influenced by atmospheric oxygen, acidified quinone solution was added to excess of potass. carbonate solution, when after the evolution of  $\text{CO}_2$  the KOH reacted as before. After the addition of acidified bichromate, the solution was extracted with ether, and gave the well-known blue colour indicating peroxide. The ether was taken from a full vessel and was previously tested for peroxide. Furthermore, quinone added to sulphite solution is reduced, the solution losing the quinone smell and developing, the process being much faster if alkali be added; but in this case the solution remains colourless. Pure  $\text{Na}_2\text{SO}_3$ , with only traces of sulphate, was employed, and hydroquinone obtained by extraction with ether. The remaining aqueous solution gave no precipitate with  $\text{BaCl}_2$  (compared with a control solution), but on evaporation and treatment with dilute acid, dithionic acid was recognised. It appears that the quinone is reduced to hydroquinone, while the sulphite is oxidised to dithionate—



It is uncertain whether this reaction is reversible, but it may be noted that K. Schaum<sup>1</sup> could obtain no satisfactory oxidation potentials for mixtures of sulphite and sulphate. It appears that the *primary* oxidation product of sulphite is dithionate,

<sup>1</sup> *Zeit. Elektrochem.*, 1901, 483; 1903, 406.

sulphate being produced as a side-product. In many cases of oxidation of sulphite dithionic acid is obtained. Thus Carpenter<sup>1</sup> gives the following table for the oxidation of sulphurous acid by metallic oxides :—

Oxide.	% Dithionate.	% Sulphate.
Iron ...	96·0	—
Manganese ...	95·0	25
Cobalt ...	36·0	64
Nickel ...	—	100

See also J. Meyer.<sup>2</sup> With quinone there seems to be but little sulphate formed, but we have made no quantitative measurements. Basset<sup>3</sup> found that dithionic acid was formed in the reduction of chromates by sulphurous acid.

The above result may explain Andresen's numbers. It is obvious that all attempts to estimate quinol which involve its oxidation to quinone must fail where alkali or sulphite are present. Thus some attempts with copper solutions were defeated. Using Soldain's copper carbonate, as with hydroxylamine, cuprous oxide was produced, but also resinous products by the further oxidation of the quinone, and but slight improvement was obtained by passing a current of steam through during the reaction to remove this body. Attempts to estimate hydroquinone in neutral or acid solution with permanganate failed, no stable end point being reached. Similar results attended the use of  $\text{FeCl}_3$ , this reaction being reversible. The use of iodine is also inadmissible, the reaction  $\text{C}_6\text{H}_4\text{O}_2 + \text{I}_2 = \text{C}_6\text{H}_4\text{O} + 2\text{I}'$  being reversible, and only available under certain conditions. It seems possible that ferricyanide may be used under certain conditions, as preliminary experiments indicate but little reversibility, while the quinone seems stable.

At present the interaction of organic reducer, sulphite, alkali, and atmospheric oxygen offers some interesting problems.

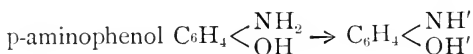
<sup>1</sup> *Chem. Soc. Trans.*, 1902, **81**. I.

<sup>2</sup> *Ber.*, 1901, **34**. 3606.

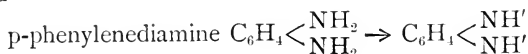
<sup>3</sup> *Trans. Chem. Soc.*, 1903, June.

Sulphites have long been added to organic developers as lessening their tendency to aërial or autoxidation, and preventing the staining of the gelatine in development. This action was ascribed to a selective oxidation of the sulphite first to sulphate, the reducer being passed by. But the investigations of Bigelow, S. W. Young, and Titoff,<sup>1</sup> have shown that the oxidation of sodium sulphite in solution is greatly retarded by the presence of small quantities of substances acting as negative catalysers. Messrs. Lumière and Seyewetz have further shown that organic developers behave in this manner, so that we have here a case of an "induced" or "coupled" reaction<sup>2</sup> in which the total reaction is retarded. While the oxidation of sodium sulphite accelerates that of sodium arsenite, here are two oxidations which both proceed far more slowly when the two substances are present together. It appears probable that this result is due to a cycle of changes. Thus, the negative catalysis with sodium sulphite has been shown to be due to the inhibition of positive catalysis (Titoff, *loc. cit.*), while the interaction of sulphite with quinones or quinonoid bodies probably accounts for the anti-oxidising action of this, as well as its prevention of staining, since the coloured bodies giving rise to this would probably be of a quinonoid structure.

The oxidation of p-phenylenediamine and p-aminophenol in ethereal solution with dry silver oxide yields di- and mono-imido-quinone respectively.<sup>3</sup> These bodies are fairly stable in aqueous solution, but decompose out of it. Their formation is readily explained on the supposition that these reducers react as dibasic acids, yielding in small quantities the ions as follows:—



and—



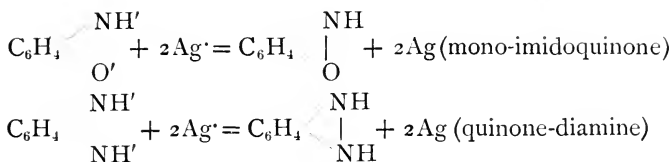
which then react with silver ions according to the equations—

<sup>1</sup> Bigelow, *Zeit. phys. Chem.*, 1898, **27**, 585; S. W. Young, *Amer. Chem. J.*, 1902, **ii**, 391; Titoff, *Zeit. phys. Chem.*, 1903, **45**, 641.

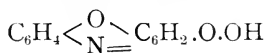
<sup>2</sup> J. W. Mellor, *Chemical Statics and Dynamics*, 1904.

<sup>3</sup> Wilstätter and Pfannensteil, *Ber.*, 1904, **37**, 4605.





the instability of these quinonoid bodies in the presence of water probably being due to a minimum of hydroxyl ions acting similarly as with quinone. Other oxidation products formed by the condensation of two or more discharged ions also behave in this way. Thus, on oxidising o-aminophenol with ferricyanide, Diepolder<sup>1</sup> obtained a mixture of triphenyl-dioxazine and 3-oxybenzolazoxindone—



which is the tautomer of phenoxazine-2-3-quinone. On treating this with caustic potash, o-aminophenol and dioxyquinone were formed, doubtless by reactions analogous to the reduction of quinone.

The view that organic reducers are oxidised in stages according to their functions as polybasic acids agrees with the fact that all these mixed phenolic and amidobenzene derivatives show their reducing power chiefly in alkaline solution, the necessity of two or more of the groups  $-\text{NH}_2$ ,  $-\text{OH}$  in the ortho- or para- position being no doubt associated with the formation of a quinonoid structure. While the acid character of the phenols is well established and stable monobasic salts are known,<sup>2</sup> the  $-\text{NH}_2$  group lowers the acid character, the aminophenols and diamines forming stable salts with strong acids. But the acidic function remains, so that these bodies are amphoteric, like hydroxylamine or hydrazine, and it will be seen that this view is in agreement with their development properties.

It is of interest to note that if the solution contain a fair proportion of sulphite, and be guarded from aerial oxidation, a considerable quantity of silver may be reduced and yet the solution remain colourless. It may be concluded that in this stage no very complicated products are formed.

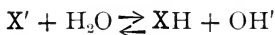
<sup>1</sup> *Ber.*, 1902, **35**. 2816.

<sup>2</sup> Hantsch, *Ber.*, 1899, **32**. 576.

PART II.—*The Dynamics and Statics of Development with Alkaline Reducers.*

The investigation of this was carried out in the same way as for development with iron salts, the characteristic plate-curve being plotted for different times of development at the various concentrations, etc., employed. The former work has shown that the velocity of development is best measured by determining  $\gamma$ , the degree of development, from the curve  $D = \gamma \log E/i$ , whence  $\gamma = dD/d \log E = \tan \theta$ . (See p. 62.) Beside this, another essential point is the constancy of  $\log i$ . The investigation of bromide and reversibility has shown that if the free energy of the reaction be materially lowered, and thereby the chemical velocity made comparable to the diffusion-velocity, then there is a shift in  $\log i$ , a regression to its true value taking place as the time of development is increased. This question, together with the conception of the *energy* of developers and its relation to the sensitometrical question of the speed of the plate, is discussed at the end of this part in the section dealing with the affinities of developers.

It has been explained in the foregoing section that all these reducing agents are weak acids, the actual reducer being the anion, the concentration of which is increased by the addition of alkali, owing to the far greater dissociation of the salts. These are subject to hydrolysis, according to the scheme—



when the mass law gives us—

$$[OH'] [XH] = K [X']$$

Now, if we have equivalent quantities of acid and base, say  $a$  grams dissolved in  $v$  liters, whereof  $x$  grams are hydrolysed, then  $a - x$  remains, and we have <sup>1</sup>—

$$\frac{x^2}{(a-x)v} = K$$

We may expect, therefore, that in the presence of sufficient

<sup>1</sup> J. Walker, *Zeit. phys. Chem.*, 1889, **4**, 319.

excess of alkali the velocity will be proportional to the reducer's concentration, with excess of reducer to that of the alkali, or faster if it depend on a polyvalent anion, while further addition will increase the velocity, owing to the diminution of hydrolysis. In the presence of equivalent quantities of reducer and alkali, the velocity should fall off faster than the dilution, owing to increased hydrolysis.

All the measurements were compared with development with ferrous oxalate, the dynamics of which had been investigated previously.<sup>1</sup> The values for the first series of plates used were as follows :—

TABLE 73.  
*n*/10 ferrous oxalate at 20°.

<i>t</i> (time in minutes).	$\gamma$ .	$K = \frac{1}{t} \log \frac{\gamma_{\infty}}{\gamma_{\infty} - \gamma}$ .
2'0	0'56	0'064
3'0	0'63	0'050
4'0	1'02	0'068
5'0	1'15	0'065
6'0	1'18	0'057
8'0	1'50	0'063
10'0	1'62	0'059
$\infty$	2'18	Mean $K = 0'061$

$$\log i = 1'25.$$

**Hydroxylamine.**—Used in the form of the hydrochloride, to which the necessary quantity of standard caustic soda was added. It has been shown that in development one molecule of  $\text{NH}_2\text{OH}$  reduces one molecule of  $\text{AgBr}$ , probably according to the equation  $\text{NH}_2\text{O}' + \text{Ag}^{\cdot} = \text{NH}_2\text{O}' + \text{Ag}$ , followed by  $2\text{-NH}_2\text{O} = \text{N}_2 + \text{H}_2\text{O}$ . The gas first forms a supersaturated solution, and then is evolved in the form of small bubbles. Owing to this, it is difficult to obtain accurate measurements of  $\gamma$  much above 1'0, and the same cause limits the technical

<sup>1</sup> *Roy. Soc. Proc.*, 1905, **74**. 475 ; and Part II. Chap. I.

application of hydroxylamine. We give the density-measurements and the characteristic curves for a few conditions to illustrate how far modifications of the developer alter the shape of the curve and the value of  $\log i$ , but it is unnecessary to give all, as they merely add to the bulk. The results as to  $\gamma$  and  $t$  are resumed in one table.

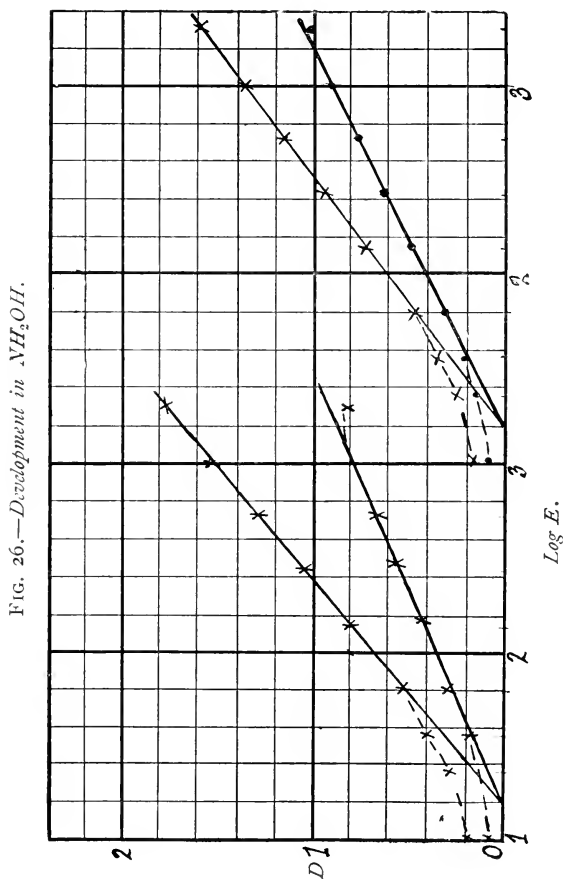


TABLE 74.

2.0 and 4.0 minutes in 0.10*n* NH<sub>2</sub>OH, 0.016*n* NaOH.

No.	Log E.	D <sub>2</sub> .	D <sub>4</sub> .
1	1.00	0.075	0.183
2	1.36	0.124	0.277
3	1.575	0.190	0.396
4	1.80	0.293	0.259
5	2.14	0.407	0.795
6	2.42	0.540	1.046
7	2.72	0.640	1.280
8	3.01	0.781	1.555
9	3.30	0.806	1.768

$\gamma_2 = 0.44.$

$\gamma_4 = 0.85.$

$\log i = 1.22.$

TABLE 75.

3.0 and 5.0 minutes in 0.05*n* NH<sub>2</sub>OH, 0.047*n* NaOH.

No.	Log E.	D <sub>3</sub> .	D <sub>5</sub> .
1	1.00	0.070	0.163
2	1.36	0.151	0.253
3	1.575	0.211	0.358
4	1.80	0.302	0.471
5	2.14	0.480	0.723
6	2.42	0.615	0.941
7	2.72	0.756	1.153
8	3.01	0.901	1.375
9	3.30	1.012	1.595

$\gamma_3 = 0.50.$

$\log i = 1.20.$

$\gamma_5 = 0.77.$

$\log i = 1.20.$

TABLE 76.

3.0 and 5.0 minutes in 0.02*n* NH<sub>2</sub>OH in 0.077*n* NaOH.

No.	Log E.	D <sub>3</sub> .	D <sub>5</sub> .
1	1.00	0.030	0.140
2	1.36	0.085	0.252
3	1.575	1.167	0.376
4	1.80	0.294	0.474
5	2.14	0.433	0.742
6	2.42	0.601	0.951
7	2.72	0.732	1.101
8	3.01	0.872	1.370
9	3.30	0.932	1.616

$\gamma_3 = 0.51.$

$\log i = 1.20.$

$\gamma_5 = 0.75.$

$\log i = 1.15.$

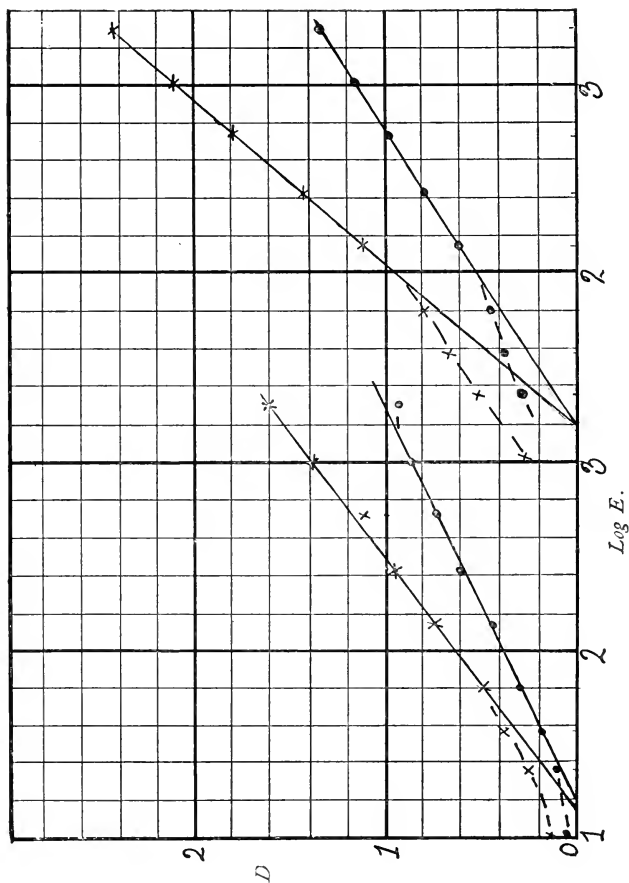
FIG. 27.—*Development with hydroxylamine.*

TABLE 77.

5'0 and 12'0 minutes in 0'01*n* NH<sub>2</sub>OH in 0'184*n* NaOH.

No.	Log E.	D <sub>5</sub> .	D <sub>12</sub> .
1	1'00	0'243	—
2	1'36	0'293	0'523
3	1'575	0'376	0'672
4	1'80	0'452	0'801
5	2'14	0'600	1'114
6	2'42	0'782	1'434
7	2'72	0'971	1'804
8	3'01	1'148	2'120
9	3'30	1'330	2'431

 $\gamma_5 = 0'63.$  $\log i = 1'20.$  $\gamma_{12} = 1'18.$  $\log i = 1'20.$ 

Generally, the density-ratios and  $\log i$  are independent of the time of development or the composition of the developer, but great excess of alkali tends to somewhat distort the curve in that the lower densities increase disproportionately. There is throughout the whole series a slight tendency for  $\log i$  to diminish with increase of alkali, *i.e.* the speed of the plate is a little raised. For the velocity measurements—

TABLE 78.

	Conc. of NH <sub>2</sub> OH.	Conc. of NaOH.	Rate of development.
A	0'010 <i>n</i>	0'087 <i>n</i>	$t$ (in mins.) 5'0, 10'0, $\infty$ $\gamma$ 0'64, 0'95, 2'18
	0'01 <i>n</i>	0'184 <i>n</i>	$t$ 5'0, 6'0, 12'0 $\gamma$ 0'63, 0'80, 1'18
	0'01 <i>n</i>	0'0335 <i>n</i>	$t$ 6'0, 10'0, 14'0, 20'0 $\gamma$ 0'47, 0'53, 0'67, 0'80
	0'020 <i>n</i>	0'077 <i>n</i>	$t$ 3'0, 5'0 $\gamma$ 0'51, 0'75
B	0'050 <i>n</i>	0'144 <i>n</i>	$t$ 0'50, 1'0, 2'0 $\gamma$ 0'35, 0'56, 1'00
	0'050 <i>n</i>	0'095 <i>n</i>	$t$ 1'0, 2'0, 2'5, 4'0 $\gamma$ 0'46, 0'70, 0'79, 0'94
	0'050 <i>n</i>	0'047 <i>n</i>	$t$ 3'0, 4'5, 5'0, 7'0 $\gamma$ 0'50, 0'75, 0'77, 0'92
	0'10 <i>n</i>	0'046 <i>n</i>	$t$ 1'0, 2'0, 3'0, 5'0 $\gamma$ 0'54, 0'80, 0'95, 1'26
C	0'10 <i>n</i>	0'016 <i>n</i>	$t$ 2'0, 2'5, 3'0, 4'0, 5'0, 6'0 $\gamma$ 0'44, 0'53, 0'65, 0'85, 0'88, 1'06

See Fig. 28 (A), (B), (C).

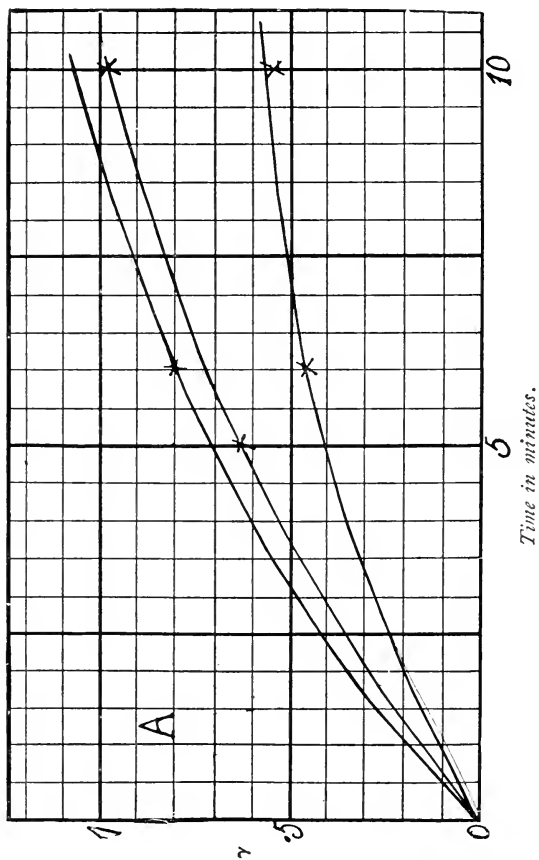
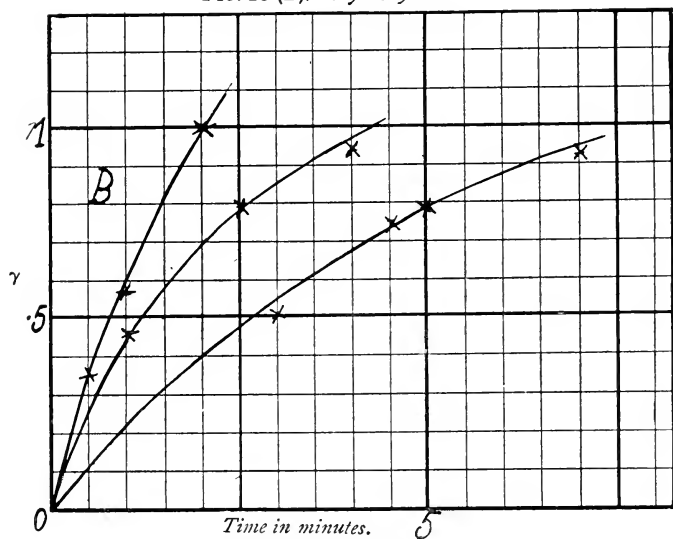
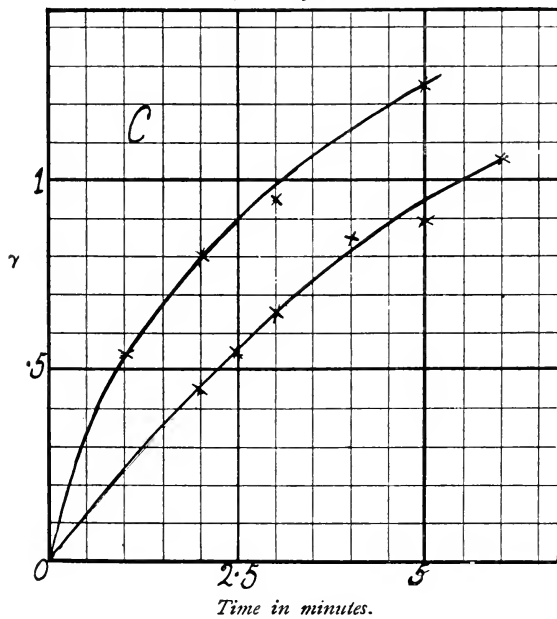
FIG. 28 (A).—*Hydroxylamine.*



FIG. 28 (B).—*Hydroxylamine.*FIG. 28 (C).—*Hydroxylamine.*

It will be seen from these data and the curves that the composition of the solution influences both the velocity and the course of development. For each concentration of  $\text{NH}_2\text{OH}$  the addition of alkali increases the velocity, but after a certain value the acceleration is very slight. This corresponds to the diminution of hydrolysis according to the mass law. In the presence of great excess of alkali, we may assume that the concentration of the salt is that of the reducer, and it will be seen that the velocity is then proportional to this. Thus, with  $0.05n$   $\text{NH}_2\text{OH}$  in  $0.144n$   $\text{NaOH}$ , the time for  $\gamma.75$  was 1.3 minutes, and in  $0.010n$   $\text{NH}_2\text{OH}$  in  $0.087n$   $\text{NaOH}$ , 6.5 minutes. It is evident that the hydrolysis is very great, since with  $n/100$   $\text{NH}_2\text{OH}$  some twenty molecules of  $\text{NaOH}$  were required to suppress it. Consequently the velocity diminishes more rapidly than the volume is increased. A solution of  $0.05n$   $\text{NH}_2\text{OH}$  in  $0.095n$   $\text{NaOH}$  was diluted twice, and nearly the same densities obtained in 2.0 and 5.0 minutes, instead of 2.0 and 4.0.

No.	Log E.	$D_2$ for $V = 1$ .	$D_5$ for $V = 2$ .
1	1.00	0.154	0.160
2	1.36	0.224	0.231
3	1.575	0.280	0.306
4	1.80	0.411	0.434
5	2.14	0.630	0.601
6	2.42	0.858	0.780
7	2.72	1.080	0.984
8	3.01	1.300	1.094

The effect of dilution is even more marked on the highest densities. It may be noted that in a very weak acid, as  $\text{NH}_2\text{OH}$ , where the hydrolysis is very great, the measurement of this by determining the concentration of free hydroxyl ions is less reliable than that of the concentration of unhydrolysed salt. Since development depends upon the concentration of the anion  $\text{NH}_2\text{O}'$ , it is possible that accurate measurements might be used to determine the degree of hydrolysis, and hence its strength as an acid.

**The Mechanism of Development and the Velocity Function.**—It has already been mentioned that for iron salts<sup>1</sup> it was deduced from the law of constant density-ratios, and from consideration of the theory of heterogeneous reactions, that the rate of development depended on the micro-diffusion or rate of supply of the reducing ion *in the film* to the affected halide; the velocity under certain conditions being given by  $dD/dt = K(D_{\infty} - D)$ , or for  $\gamma$ ,  $d\gamma/dt = K(\gamma_{\infty} - \gamma)$ , by integration,  $\frac{1}{t} \log \frac{\gamma_{\infty}}{\gamma_{\infty} - \gamma} = K$ , a constant which was verified for iron salts. (See also Table 73.) The application of this to hydroxylamine showed that it held under certain restricted conditions. Owing to the great velocity of development, the "invasion" of the developer ceases to be rapid compared with the permeation in the film (*vide* p. 132), so that concentrated solutions give decreasing values of  $K$ , while with solutions much below  $n/40$  the amount of reducer oxidised is no longer small compared with the total amount. On the whole, the most concordant results were obtained with excess of reducer present. The following results are given to compare the velocity with ferrous oxalate:—

TABLE 79.  
0.10*n* NH<sub>2</sub>OH in 0.016*n* NaOH.

$t$ (in minutes).	$\gamma$ .	$K = \frac{1}{t} \log \frac{\gamma_{\infty}}{\gamma_{\infty} - \gamma}$ .
2.0	0.44	0.0490
2.5	0.53	0.0485
3.0	0.65	0.0510
4.0	0.85	0.0530
5.0	0.88	0.0450
6.0	1.06	0.0482
$\infty$	—	$K, \text{ mean} = 0.0491$

Assuming the excess of NH<sub>2</sub>OH completely suppressed the hydrolysis, we may reckon the concentration of the reducing ion as [NH<sub>2</sub>O' = 0.016*n*. For 0.10*n* the velocity would

<sup>1</sup> *Roy. Soc. Proc.*, 1905, **74**, 457; and Part II. Chap. I. p. 62.

be 0.306, compared with 0.061 for 0.10*N* ferrous oxalate. For another series we have—

TABLE 80.  
0.01*N* NH<sub>2</sub>OH in 0.184*N* NaOH.

<i>t</i> (in minutes).	$\gamma$ .	$K = \frac{1}{t} \log \frac{\gamma_{\infty}}{\gamma_{\infty} - \gamma}$ .
5.0	0.63	0.030
6.0	0.80	0.033
12.0	1.18	0.028
$\infty$	—	K, mean = 0.0303

Hence, for 0.10*N* NH<sub>2</sub>O', 0.303, in good agreement with the value found when the hydrolysis was suppressed by excess of NH<sub>2</sub>OH. The relative velocities of development by the NH<sub>2</sub>O' ion and the Fe(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>" ion are as 0.305 to 0.061, or 5 to 1 at 20°.

**Viscosity of Solution and Development.**—Experiments on the addition of alcohol to the developer showed that the viscosity had little or no influence on the rate of development. The developer was 0.05*N* NH<sub>2</sub>OH in 0.047*N* NaOH.

(*a*) with no alcohol.      (*b*) with 25 % ethyl alcohol.

*t* . . . 3.0, 5.0

4.5, 7.0

$\gamma$  . . . 0.50, 0.77

0.75, 0.92

K = 0.0375

K = 0.0375

The values of  $\gamma$  lie on the same curve, and the velocities are identical. In mixtures of ethyl alcohol and water the values obtained by A. E. Dunstan<sup>1</sup> were  $\eta = 0.00891$  for pure water, and  $\eta = 0.01851$  for 24.7 per cent. by weight of alcohol. Hence, approximately doubling the viscosity of the solution did not influence the velocity, which agrees with the view that in general the rate of entry of the developer into the film is much faster than the rate of development.

**The Developing Equivalence of the Alkalis.**—Experiments were made to determine the relative development values of KOH, NaOH, LiOH, and K<sub>2</sub>CO<sub>3</sub>. These measurements

<sup>1</sup> *Chem. Soc. Trans.*, 1904, 85. 817.

were made with a different batch of plates to those in the foregoing, the value of  $\gamma_{\infty}$  being 2.50. The solutions of alkali were titrated against standard sulphuric acid, and quantities equivalent to 10 c.c. *normal* alkali taken in each case. The developer was composed of 5 c.c. *n*  $\text{NH}_2\text{OH}.\text{HCl}$ , 10.0 c.c. *n* alkali to 100 c.c. with water. In the case of  $\text{K}_2\text{CO}_3$  the hydrochloride was just neutralised with  $\text{KOH}$ , then 10.0 c.c. of molar  $\text{K}_2\text{CO}_3$  added.

TABLE 81.

		NaOH.			
Time in minutes . .		2'0.	3'0.	4'0.	5'0.
No.	Log E.	D <sub>2</sub> .	D <sub>3</sub> .	D <sub>4</sub> .	D <sub>5</sub> .
1	1'00	0'058	0'080	0'135	0'160
2	1'36	0'138	0'244	0'359	0'390
3	1'575	0'224	0'382	0'574	0'594
4	1'80	0'386	0'604	0'810	0'916
5	2'14	0'596	0'865	1'120	1'233
6	2'42	0'748	1'137	1'432	1'550
7	2'72	0'852	1'387	1'724	1'860
8	3'01	1'020	1'640	2'034	2'160
9	3'30	1'179	1'854	2'312	2'470
	$\gamma =$	0'43	0'83	1'01	1'08

TABLE 82.

		KOH.		LiOH.	
Time in minutes . .		2'0.	4'0.	2'0.	4'0.
No.	Log E.	D <sub>2</sub> .	D <sub>4</sub> .	D <sub>2</sub> .	D <sub>4</sub> .
1	1'00	0'056	0'134	0'052	0'156
2	1'36	0'140	0'377	0'147	0'384
3	1'575	0'231	0'540	0'248	0'552
4	1'80	0'426	0'782	0'422	0'748
5	2'14	0'692	1'006	0'658	1'020
6	2'42	0'880	1'344	0'836	1'340
7	2'72	1'068	1'600	1'029	1'624
8	3'00	1'233	1'816	1'104	1'920
9	3'30	1'357	2'160	1'344	2'230
	$\gamma =$	0'54	0'96	0'56	0'97

It is evident from the densities alone that the velocity is the *same* for equimolecular concentrations of NaOH, LiOH, and KOH, *i.e.* the developing equivalence of the alkalis is the same as their affinity-constants as bases, the effect depending only on the concentration of hydroxyl ions.<sup>1</sup> For the mean velocity-constant,  $K = \frac{1}{t} \log \frac{\gamma_{\infty}}{\gamma_{\infty} - \gamma}$ , the results given in the next table were obtained.

TABLE 83.

NaOH.			KOH.			LiOH.		
<i>t.</i>	$\gamma$ .	<i>k.</i>	<i>t.</i>	$\gamma$ .	<i>k.</i>	<i>t.</i>	$\gamma$ .	<i>k.</i>
2'0	0'43	0'040	2'0	0'54	0'058	2'0	0'56	0'055
3'0	0'83	0'062						
4'0	1'01	0'056	4'0	0'96	0'053	4'0	0'97	0'053
5'0	1'08	0'049						
$\infty$	2'50	—	$\infty$	2'50				

K = 0'052.

K = 0'056.

K = 0'054.

The values obtained for  $m/10$  K<sub>2</sub>CO<sub>3</sub> were—

TABLE 84.

Time in minutes ...		K <sub>2</sub> CO <sub>3</sub> .			
		12'5.	21'5.	25'0.	45'0.
No.	Log E.	D <sub>1</sub> .	D <sub>2</sub> .	D <sub>3</sub> .	D <sub>4</sub> . <sup>2</sup>
1	1'00	0'072	0'050	0'080	0'020
2	1'36	0'092	0'179	0'230	0'108
3	1'575	0'138	0'303	0'388	0'232
4	1'80	0'218	0'460	0'566	0'479
5	2'14	0'361	0'671	0'852	0'892
6	2'42	0'415	0'884	1'080	1'215
7	2'72	0'547	1'080	1'296	1'600
8	3'01	0'671	1'200	1'560	1'920
9	3'30	0'759	1'300	1'768	2'312
	$\gamma$ =	0'36	0'66	0'81	1'19
	K =	0'0055	0'0062	0'0067	0'0062

Mean, K = 0'0062.

<sup>1</sup> Nernst, *Theoret. Chem.*, 4<sup>te</sup> Alge., 512.

<sup>2</sup> The lower values of D obtained here and the shift in log *i* is due to a veil of dichroic fog (pink) over the unexposed portion.

From these we have—

$$\begin{array}{ll} 0.05N \text{ KOH} & K = 0.054 \\ 0.10N \text{ K}_2\text{CO}_3 & K = 0.0062 \end{array}$$

Assuming that the velocity is proportional to the concentration of hydroxyl ions, the hydrolysis of  $\text{K}_2\text{CO}_3$  in decinormal solution is calculated to be 5.4 per cent. For  $\text{Na}_2\text{CO}_3$  Shields,<sup>1</sup> by the saponification with ethyl acetate, found 3.17 per cent.; while Koelichen,<sup>2</sup> from the velocity of acetone condensation, got 2.2 per cent. The determination of the hydrolysis of carbonates and similar salts by development with  $\text{NH}_2\text{OH}$  is somewhat vitiated by the alkalinity of the  $\text{NH}_2\text{OH}$  itself. The hydroxyl ions furnished by this will increase the velocity and give too high a value. But the result is sufficiently near to show that the developing value of carbonates and similar salts simply depends upon their hydrolytic dissociation and the hydroxyl ions furnished thereby.

**Influence of Temperature.**—Developer, 0.05N  $\text{NH}_2\text{OH}$  in 0.047N  $\text{NaOH}$ .

At 20° K = 0.054, at 11.5° K = 0.030; hence the temperature coefficient, or  $\frac{K + 10^\circ}{K} = 2.1$ .

**Hydroquinone or Quinol.**—As a developer, has certain marked characteristics. In photographic terminology, the image appears somewhat slowly, but then gains in strength with increasing rapidity. This was borne out to some extent by the measurements, which indicate an initial induction with this developer. In some cases, especially with great defect of alkali, there is a regression of the inertia, the value of  $\log i$  not reaching the ferrous oxalate value till a high degree of development is reached, the lower tones being retarded at the start. This effect is also produced by lowering the temperature, whilst, as will be shown later, the effect of bromide is very great with this developer. All these facts agree with an initially low chemical velocity, the potential of the system being raised as metallic silver is deposited, and as the quinone first formed is decomposed by alkali and sulphite (see

<sup>1</sup> *Zeit. phys. Chem.*, 1893, **12**, 167.

<sup>2</sup> *Ibid.*, 1900, **33**, 173.

pp. 152, 153). Owing to this initial sluggishness some difficulty was experienced in obtaining concordant and reliable measurements for low values of  $\gamma$ , since the law of constant density-ratios is, as mentioned above, frequently not followed. Illustrative curves of the peculiarities of quinol are given, besides a summary of all the data for velocity measurements.

TABLE 85.  
0.05*m* quinol in 0.0485*N* NaOH.

Time in minutes ...		3.0.	6.0.	7.0.
No.	Log E.	D <sub>3.</sub>	D <sub>6.</sub>	D <sub>7.</sub>
1	1.00	0.040	0.044	0.085
2	1.36	0.075	0.100	0.154
3	1.575	0.108	0.199	0.292
4	1.80	0.190	0.462	0.506
5	2.14	0.306	0.705	0.828
6	2.42	0.450	0.936	1.104
7	2.72	0.564	1.200	1.438
8	3.01	0.719	1.476	1.670
9	3.30	0.824	1.758	1.906
	$\gamma =$	0.41	0.89	1.00

$$\log i = 1.25.$$

TABLE 86.  
0.10*m* quinol in 0.0485*N* NaOH.

Time in minutes ...		4.0.	4.5.	6.0.	9.0.
No.	Log E.	D <sub>4.</sub>	D <sub>4.5.</sub>	D <sub>6.</sub>	D <sub>9.</sub>
1	1.000	0.030	0.047	0.082	0.096
2	1.36	0.078	0.086	0.092	0.169
3	1.575	0.116	0.148	0.172	0.286
4	1.80	0.182	0.242	0.249	0.512
5	2.14	0.286	0.346	0.416	0.828
6	2.42	0.366	0.477	0.544	1.089
7	2.72	0.481	0.600	0.705	1.390
8	3.01	0.564	0.768	0.880	1.600
9	3.30	0.725	0.970	1.062	1.860



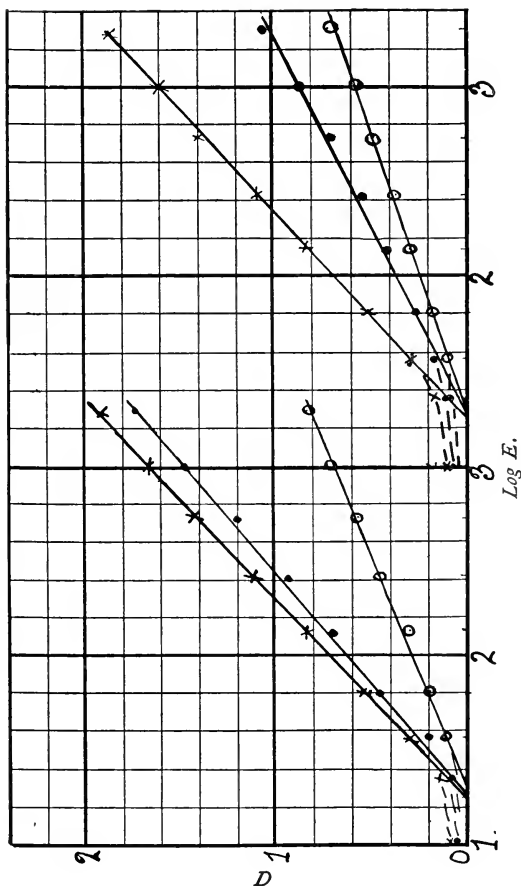
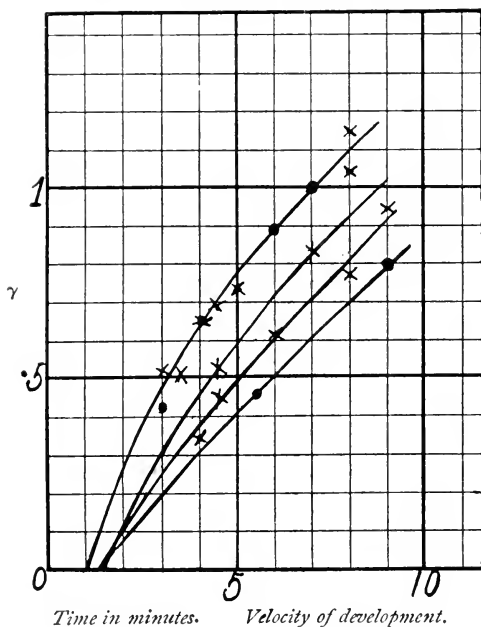
FIG. 29.—Development in  $N/20$  quinol and  $N/10$  quinol.

TABLE 87.

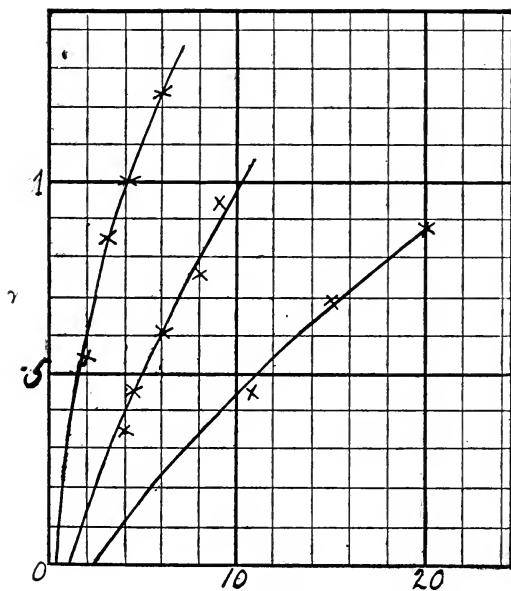
*Velocity Measurements with Quinol.*Concentration of alkali, constant; of quinol, varied.  $t_a$  = time of appearance;  $t$  = time in minutes.

$C_{\text{quinol}}$	$C_{\text{NaOH}}$	Rate of development.	$T_a$ , mins.
0.015 <i>n</i>	0.0485 <i>n</i>	$t$ 5.5, 9.0 $\gamma$ 0.45, 8.0	1.3
0.025 <i>n</i>	0.0485 <i>n</i>	$t$ 3.0, 4.0, 5.0, 8.0 $\gamma$ 0.515, 0.645, 0.735, 1.15	1.0
0.025 <i>n</i>	0.0485 <i>n</i>	$t$ 3.5, 4.5, 5.0, 8.0 $\gamma$ 0.50, 0.68, 0.73, 1.04	1.0
0.050 <i>n</i>	0.0485 <i>n</i>	$t$ 3.0, 4.0, 6.0, 7.0 $\gamma$ 0.41, 0.66, 0.89, 1.00	1.0
0.100 <i>n</i>	0.0485 <i>n</i>	$t$ 4.0, 4.5, 6.0, 8.0, 9.0 $\gamma$ 0.34, 0.45, 0.61, 0.76, 0.945	1.3
0.200 <i>n</i>	0.0485 <i>n</i>	$t$ 4.5, 7.0 $\gamma$ 0.515, 0.835	1.5

FIG. 30.—*Variation of quinol concentration.*

Concentration of quinol constant at 0.100*N*.

$C_{\text{quinol}}$	$C_{\text{NaOH}}$	Rate of development.	$T_a$
0.100 <i>N</i>	0.0194 <i>N</i>	$t$ 11.0, 15.0, 20.0, 26.0 $\gamma$ 0.44, 0.69, 0.875, 1.04	mins. 2.51
0.100 <i>N</i>	0.097 <i>N</i>	$t$ 2.0, 3.0, 4.0, 6.0 $\gamma$ 0.54, 0.85, 1.00, 1.23	0.51
0.100 <i>N</i>	0.0485 <i>N</i>	$t$ 4.0, 4.5, 6.0, 8.0, 9.0 $\gamma$ 0.34, 0.45, 0.61, 0.75, 0.945	1.3

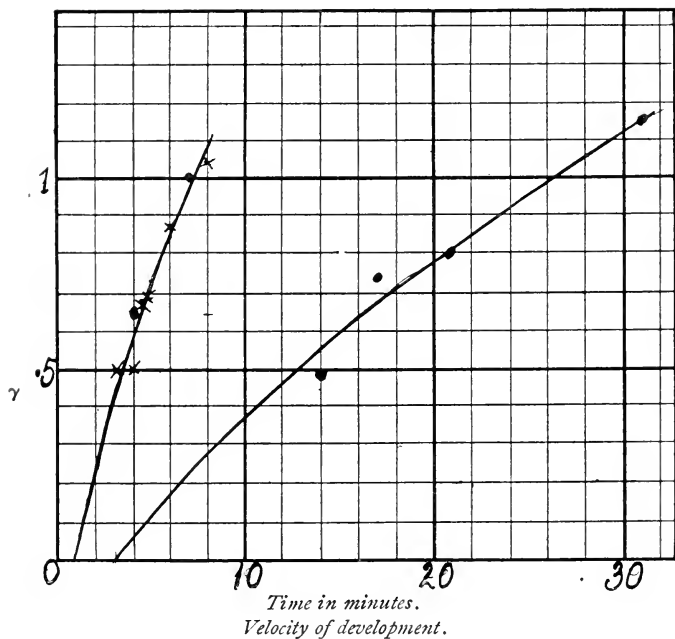
FIG. 31.—Variation of alkali with  $N/10$  quinol.

Time in minutes.

Velocity of development with quinol.

Concentration of quinol constant at 0.025*n*.

$C_{\text{quinol}}$	$C_{\text{NaOH}}$	Rate of development.	$T_a$ .
0.025 <i>n</i>	0.194 <i>n</i>	$t$ 4.0, 7.0 $\gamma$ 0.65, 1.00	mins. 0.95
0.025 <i>n</i>	0.097 <i>n</i>	$t$ 4.0, 5.0, 6.0, 8.0 $\gamma$ 0.50, 0.685, 0.87, 1.03	1.00
0.025 <i>n</i>	0.0485 <i>n</i>	$t$ 3.5, 4.5, 5.0, 8.0 $\gamma$ 0.50, 0.68, 0.78, 1.04	1.00
0.025 <i>n</i>	0.0194 <i>n</i>	$t$ 14.0, 17.0, 21.0, 31.0 $\gamma$ 0.48, 0.73, 0.79, 1.15	3.00

FIG. 32.—Alkali with  $N/40$  quinol.

The experiments with constant alkali and increasing quantities of quinol give a curious result. Up to  $m/40$  quinol

the velocity increases proportionately to the quinol concentration. Thus interpolating for the same value of  $\gamma$ —

$\gamma$ .	Time in 0.015 <i>N</i> .	Time in 0.025 <i>N</i> .	Ratio.
0.3	4.0 mins.	2.3 mins.	1.73
0.4	5.0 „	2.9 „	1.72
0.5	6.0 „	3.5 „	1.71
0.8	9.0 „	5.4 „	1.66

Ratio of concentrations, 1.67.

But the velocity reaches a maximum for 0.025*N* quinol, the values for 0.05*N* being identical; 0.10 shows a minimum, while with 0.20*N* the values rise again somewhat, but not to equal 0.25*N*. It is evident that a certain excess of quinol at high concentrations lowers the velocity. This effect on the  $\gamma, t$  curve must be kept distinct from any effect in raising  $\log i$ , and so additionally depressing the density.

**Velocity and Alkali Concentration.**—With 0.025*N* quinol further addition of alkali above 0.05*N* NaOH had little or no accelerating influence (see Fig. 32). The relation of the velocities with 0.0194*N* NaOH and 0.0485*N* NaOH gave—

TABLE 88.

$\gamma$ .	$t$ for 0.0194 <i>N</i> .	$t$ for 0.0485 <i>N</i> .	Ratio.
Appearance	3.00 mins.	1.00 mins.	3.00
0.50	13.2 „	3.2 „	4.10
0.70	18.1 „	4.3 „	4.20
0.80	21.0 „	5.1 „	4.10
1.00	27.0 „	7.0 „	3.90

The ratio of concentrations is 2.5, so the velocity increases somewhat faster than this. It attains a maximum for one molecule of quinol to two molecules of NaOH, which was also

found when varying the quinol; this agrees with the view that the developing ion is  $C_6H_4O_2''$  from the dibasic salt  $C_6H_4(ONa)_2$ , but the fact that further addition of alkali has little or no influence on the velocity indicates that the hydrolysis is small. This is surprising, as quinol is only a very weak acid, according to conductivity measurements.<sup>1</sup> This behaviour is similar to that of Hantsch's pseudo-acids,<sup>2</sup> *i.e.* weak acids, whose salts show abnormally low hydrolysis. Hantsch showed that this is characteristic of tautomeric change in the acid molecule, and it is of interest to note that Baly and Ewbank,<sup>3</sup> from their spectroscopic study of quinol in solution, attribute tautomerism (labile hydrogen) to this body.

TABLE 89.

Alkali with 0.100*n* quinol. Interpolating times for equal  $\gamma$  in (1) 0.0194*n* NaOH; (2) 0.0485*n*; (3) 0.097*n*.

$\gamma$ .	$t_1$ .	$t_2$ .	$t_3$ .	$R_1$ .	$R_2$ .	$R_3$ .
Appearance	2.5	1.0	0.5	5.0	2.0	1.0
0.4	9.0	4.0	1.4	6.4	2.86	1.0
0.5	11.2	5.0	1.7	6.6	2.94	1.0
0.7	15.4	6.8	2.4	6.4	2.83	1.0
1.0	24.5	10.0	4.0	8.1	2.50	1.0

It will be seen that here the velocity increases only slightly more rapidly than the concentration of the alkali. While the developing ion is the divalent  $C_6H_4O_2''$  it is probable that at certain stages the velocity depends upon the rate of supply of the univalent  $C_6H_5O_2'$ , which with alkali furnish relatively few  $C_6H_4O_2''$  ions. On the balance between these two depend possibly some of the anomalies with quinol development.

<sup>1</sup> R. Bader, *Zeit. phys. Chem.*, **6**, 291.

<sup>2</sup> *Ber.* 1899, **32**, 576.

<sup>3</sup> *Chem. Soc. Trans.*, 1905, **87**, 1354.

**The Velocity Function.**—For the steady period the results agree fairly well with the exponential formula. For 0.025*n* quinol in 0.0485*n* NaOH we have for comparison with ferrous oxalate—

TABLE 90.

<i>t</i> (in minutes).	$\gamma$ .	$K = 1/t \log \gamma_{\infty}/\gamma_{\infty} - \gamma$ .
3.0	0.51	0.038
3.5	0.50	0.033
4.0	0.65	0.038
4.5	0.68	0.036
5.0	0.73	0.036
8.0	1.10	0.038
$\infty$	2.18	Mean, $K = 0.0365$

For 0.10*n* quinol with maximum alkali  $K$  is calculated from this as 0.146. Actually for 0.10*n* quinol in 0.097*n* NaOH the values obtained were—

TABLE 91.

<i>t</i> (in minutes).	$\gamma$ .	$K$ .
2.0	0.54	0.062
3.0	0.85	0.071
4.0	1.00	0.066
6.0	1.23	0.060
$\infty$	2.18	Mean, $K = 0.065$

With two molecules of alkali,  $K = 0.130$  in sufficiently good agreement with the foregoing result. Compared with  $n/10$  ferrous oxalate, we have  $K$  quinol = 0.146,  $K$  ferrous oxalate = 0.061, so that, per gram-molecule, quinol develops 2.4 times as fast, but on a basis of equal reducing power, 1.2 times ferrous oxalate.

## Influence of Temperature.—

FIG. 33.—Development at 11° C.

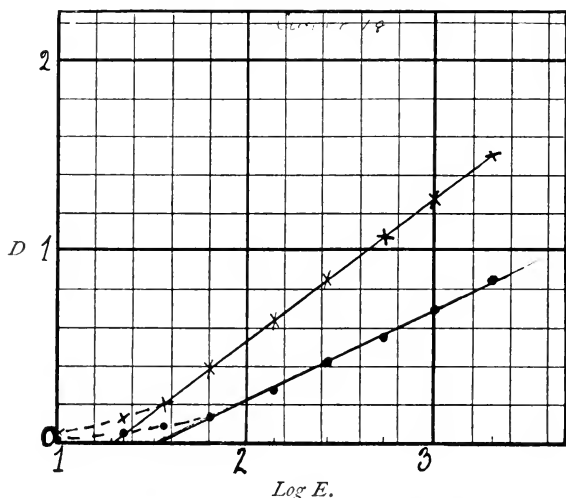
8 and 13 minutes at 11° in  $N/20$  quinol.

TABLE 91A.

At 11°0' in 0.05*n* quinol in 0.0485*n* NaOH.

No.	Log E.	D, 8 minutes.	D, 13 minutes.
1	1.00	0.015	0.053
2	1.36	0.045	0.124
3	1.575	0.089	0.208
4	1.80	0.147	0.388
5	2.14	0.272	0.630
6	2.42	0.412	0.852
7	2.72	0.540	1.060
8	3.01	0.713	1.290
9	3.30	0.852	1.512

8.0 mins.,  $\log i = 1.55$        $\gamma = 0.483$   
 13.0 " " = 1.30       $\gamma = 0.750$   
 ∞ " " = 1.25       $\gamma = 2.18$

K at 20° = 0.036, K at 11° = 0.0138, hence the temperature coefficient  $\frac{K + 10^\circ}{K} = 2.8$ . The marked regression of the



inertia at the lower temperature indicates a low free energy in the reaction.

**Influence of Sulphite.**—Experiment showed that variation in the quantity of sulphite had no influence on the density, save in preventing staining: the quantity was adjusted to the concentration of the reducer.

**"Fog."**—In common with other alkaline reducers, excess of alkali tends to the production of normal black fog. The cause of this is dealt with later.

**Para-aminophenol.**—Photographically used as "rodinal." For these experiments the hydrochloride was used, after purification by precipitation with pure hydrochloric acid and drying *in vacuo* over lime. The colourless solution keeps fairly well without sulphite. The addition of this to a concentrated solution precipitates the free base  $C_6H_4\begin{smallmatrix} \text{NH}_2 \\ \text{OH} \end{smallmatrix}$ , which redissolves on the addition of alkali forming a salt. P-aminophenol is an amphoteric electrolyte similar to hydroxylamine. Its salts, with strong acids, may be titrated with caustic soda, using phenolphthalein as an indicator. It is probable that development is mainly due to the divalent ion  $C_6H_4\begin{smallmatrix} \text{NH}' \\ \text{O}' \end{smallmatrix}$  (see Part I.), but also to some extent to the monovalent ion  $C_6H_4\begin{smallmatrix} \text{O}' \\ \text{NH}_2 \end{smallmatrix}$ , existing in relatively greater concentration, two discharged ions condensing to form 1·4 azoxindones, so that the reducing power would vary between 1 and 2, according to the dilution and composition of the solution. Andresen finds that one molecule reduces 1·7 mols. AgBr.

The developing characteristics of the aminophenols and their derivatives are just the opposite to those of quinol. The image appears very rapidly, there being no lag in the lower tones, and in consequence the law of constant density-ratios is followed from the start. But the velocity diminishes very rapidly with the time, and more so for the highest densities, resulting sometimes in a certain distortion of the curve for the high degrees of development. Moreover, the course of development varies considerably with the dilution and composition of the solution, so that comparable velocity measurements on an even scale are difficult to obtain.

The following tables and curves illustrate the action of development on the characteristic curve. It will be seen that rodinal gives very satisfactory negatives at a low degree of development, there being no regression of the inertia even for such low factors as  $\gamma^2$ .

TABLE 92.

0.02*n* p-aminophenol in 0.015*n* NaOH.

Time in minutes ...		1.0.	2.0.	3.0.	5.0.
No.	Log E.	D <sub>1</sub> .	D <sub>2</sub> .	D <sub>3</sub> .	D <sub>4</sub> .
1	1.00	0.010	0.015	0.039	0.054
2	1.36	0.047	0.070	0.150	0.190
3	1.575	0.097	0.153	0.260	0.352
4	1.80	0.190	0.274	0.404	0.565
5	2.14	0.306	0.446	0.602	0.845
6	2.42	0.377	0.556	0.816	1.110
7	2.72	0.492	0.682	1.025	1.364
8	3.01	0.566	0.806	1.186	1.570
9	3.30	0.647	0.924	1.344	1.810
	$\gamma =$	0.297	0.43	0.64	0.865
	$\log i =$	1.10			

TABLE 93.

0.020*n* p-aminophenol in 0.025*n* NaOH.

Time in minutes ...		0.50.	1.0.	2.0.	5.0.
No.	Log E.	D <sub>1/2</sub> .	D <sub>1</sub> .	D <sub>2</sub> .	D <sub>5</sub> .
1	1.00	0.020	0.048	0.022	0.040
2	1.36	0.078	0.133	0.120	0.168
3	1.575	0.139	0.222	0.230	0.319
4	1.80	0.210	0.382	0.428	0.644
5	2.14	0.286	0.483	0.674	1.006
6	2.42	0.351	0.608	0.865	1.276
7	2.72	0.442	0.707	1.056	1.580
8	3.01	0.496	0.824	1.244	1.828
9	3.30	0.560	0.975	1.438	2.120
	$\gamma =$	0.27	0.46	0.68	1.03
	$\log i =$	1.10			

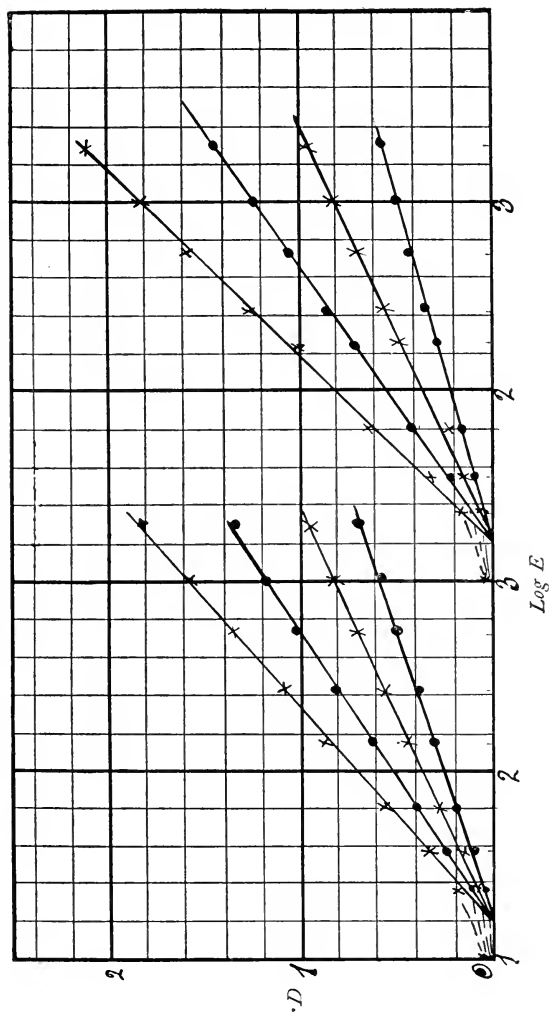
FIG. 34.— $N/50$  *p*-aminophenol in  $N/60$  and  $N/40$   $\text{NaOH}$ .

TABLE 94.  
0.10*N* *p*-aminophenol in 0.10*N* NaOH.

Time in minutes ...		1'o.	2'o.	3'o.	6'o.
No.	Log E.	D <sub>1</sub> .	D <sub>2</sub> .	D <sub>3</sub> .	D <sub>6</sub> .
1	1'00	0'043	0'085	0'136	0'165
2	1'36	0'168	0'307	0'420	0'460
3	1'575	0'292	0'525	0'701	0'748
4	1'80	0'528	0'828	1'058	1'169
5	2'14	0'820	1'163	1'550	1'745
6	2'42	1'011	1'570	2'000	2'180
7	2'72	1'233	1'906	2'400	2'500
8	3'01	1'480	2'200	2'766	2'894
9	3'30	1'734	2'470	3'040	3'176
	$\gamma =$	0'79	1'25	1'60	1'80
	$\log i =$	1'15	1'15	1'15	1'15

FIG. 35.— $N/10$  *p*-aminophenol.

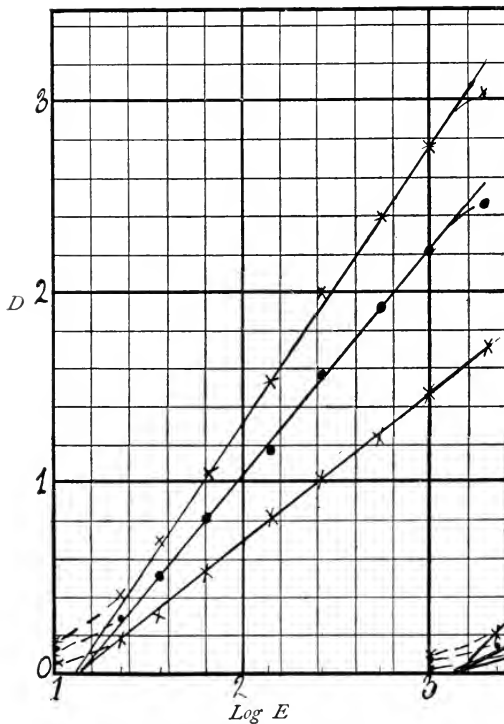


TABLE 95.

Dilution effect. 0.025*n* p-aminophenol in 0.025*n* NaOH.

Time in minutes ...		0.50.	1.0.	2.5.	5.0.
No.	Log E.	D <sub>1/2</sub> .	D <sub>1</sub> .	D <sub>2.5</sub> .	D <sub>5</sub> .
1	1.00	0.015	0.020	0.060	0.078
2	1.36	0.053	0.105	0.144	0.196
3	1.575	0.109	0.213	0.251	0.364
4	1.80	0.190	0.330	0.358	0.472
5	2.14	0.267	0.468	0.732	1.016
6	2.42	0.330	0.622	0.936	1.309
7	2.72	0.422	0.732	1.163	1.630
8	3.01	0.477	0.865	1.372	1.890
9	3.30	0.594	1.056	1.590	2.068
	$\gamma =$	0.27	0.50	0.74	1.05
	$\log i =$	1.15	1.15	1.15	1.15

The following are the complete data obtained for the influence of concentration, alkali, and temperature on the velocity :—

TABLE 96.

Effect of alkali.

Conc. of p-amino-phenol.	Conc. of NaOH.	Rate of development.	
0.020 <i>n</i>	0.015 <i>n</i>	<i>t</i> 1.0, 2.0, 3.0, 5.0 $\gamma$ 0.297, 0.43, 0.64, 0.865	$\infty$ 2.18
0.020 <i>n</i>	0.025 <i>n</i>	<i>t</i> 0.50, 1.0, 2.0, 5.0 $\gamma$ 0.27, 0.46, 0.68, 1.03	,, ,,
0.050 <i>n</i>	0.050 <i>n</i>	<i>t</i> 0.50, 2.0, 4.0, 8.0 $\gamma$ 0.42, 0.79, 1.25, 1.50	,, ,,
0.050 <i>n</i>	0.020 <i>n</i>	<i>t</i> 0.50, 1.0, 2.0, 4.0, 6.0 $\gamma$ 0.32, 0.63, 1.00, 1.10, 1.32	,, ,,

TABLE 97.

Effect of dilution.

Conc. of p-amino-phenol.	Conc. of NaOH.	Rate of development.
0'10 <i>n</i>	0'10 <i>n</i>	<i>t</i> 1'0, 2'0, 3'0, 6'0 <i>γ</i> 0'79, 1'25, 1'60, 1'80
0'05 <i>n</i>	0'05 <i>n</i>	<i>t</i> 0'50, 2'0, 4'0, 8'0 <i>γ</i> 0'42, 0'79, 1'25, 1'50
0'025 <i>n</i>	0'025 <i>n</i>	<i>t</i> 0'50, 1'0, 2'0, 2'5, 5'0 <i>t</i> 0'27, 0'50, 0'70, 0'74, 1'04

Temperature for 0'05*n* p-aminophenol in 0'02*n* NaOH.

At 11° ...	<i>t</i> 1'5, 3'0, <i>γ</i> 0'62, 0'81	$\log i = 1'15$
At 20° ...	<i>t</i> 0'50, 1'0, 2'0 <i>γ</i> 0'32, 0'63, 1'00	$\log i = 1'15$

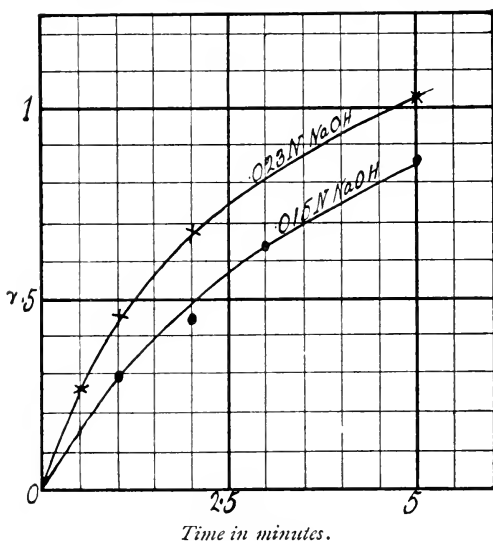
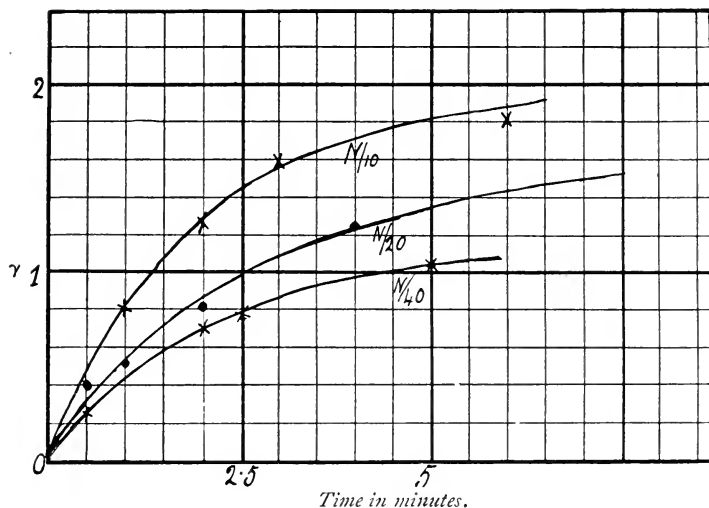
FIG. 36.—Effect of alkali on velocity with *N*/50 *p*-aminophenol.

FIG. 37.—Dilution and velocity.



From these data it will be seen that the velocity is approximately proportional to the alkali concentration with constant excess of reducer, and nearly inversely as the dilution when the alkali and reducer are present in equimolecular proportions, while the temperature coefficient  $\frac{K + 10^\circ}{K} = 1.5$ .

Again, with equimolecular quantities, the following results were obtained for the initial velocities by the "time of appearance" (*vide* p. 87) :—

TABLE 98.  
Time of appearance and concentration.

$T_a$ in seconds.	Volume, V.	$T_a/V$ .	Concentration.
5'0	1'0	5'00	$m/20$
10'3	2'0	5'15	$m/40$
21'0	4'0	5'25	$m/80$
39'6	8'0	4'90	$m/160$
81'0	16'0	5'08	$m/320$
247'4	32'0	7'75	$m/640$

And for  $m/200$ , 30.2 secs.,  $m/400$ , 74.1 secs., with a different exposure. Thus the initial velocity is proportional to the concentration down to about  $m/400$ , and then falls off more rapidly, either owing to increased hydrolysis or diminished reduction potential.

**The Velocity Function.**—As may be seen from the curves, etc., the velocity falls off very rapidly with the time, and much more than with ferrous oxalate or quinol. The exponential formula only holds for a very short stage of development, the values of  $K$  then steadily diminishing. But that the development follows the same function of the density of the image is shown by the constancy of the density-ratios. The reason for the altered course of development seems to be the following. The rate of development—the process in the film—is so rapid that it becomes as fast or faster than the invasion (see p. 132) of the developer. This cause of divergence was already indicated with hydroxylamine, development with which approaches somewhat to that with *p*-aminophenol, as might be expected from their similarity in structure. This view is supported by the fact that increased stirring seems to have an effect in increasing the velocity in the latter stages (compare Fixation).

**Comparison with Ferrous Oxalate.**—Owing to this divergence it is difficult to compare the velocity with that of ferrous oxalate, since the ratio will depend upon the stage of development at which the comparison is made. For dynamical purposes it appears best to choose the early stages of maximum velocity, and the comparison for  $\gamma.5$  (about 20 per cent. of the reaction) gave the following result at 20°, though for photographic purposes  $\gamma = 1.00$  would be best :—

$K$ for 0.020 <i>N</i> <i>p</i> -aminophenol	= 0.110
„ 0.10 <i>N</i> <i>p</i> -aminophenol	= 0.550
„ 0.10 <i>N</i> ferrous oxalate	= 0.061

Whence, per gram-molecule, *p*-aminophenol develops some nine times as fast as ferrous oxalate.

The great initial velocity, the absence of any regression of the inertia even at low temperatures, the low temperature



coefficient, all point to a high reduction potential. This is confirmed by the slight bromide sensitiveness of this reducer.

**Methyl-p-aminophenol or Metol.**—Used in the form of the sulphate  $C_6H_4 \begin{smallmatrix} \text{OH} \\ \text{HN.CH}_3 \end{smallmatrix} \cdot \frac{H_2SO_4}{2}$

TABLE 99.  
0.05*n* metol in 0.02*n* NaOH.

Time in minutes ...		0.50.	1.0.	1.5.	2.0.
No.	Log E.	D <sub>0.50</sub> .	D <sub>1</sub> .	D <sub>1.5</sub> .	D <sub>2</sub> .
1	1.00	0.033	0.045	0.048	0.067
2	1.36	0.063	0.076	0.108	0.123
3	1.575	0.123	0.148	0.245	0.321
4	1.80	0.206	0.258	0.388	0.468
5	2.14	0.351	0.438	0.632	0.743
6	2.42	0.462	0.584	0.803	0.952
7	2.72	0.570	0.720	1.020	1.200
8	3.01	0.680	0.862	1.196	1.416
9	3.30	0.801	1.010	1.401	1.660
	γ =	0.40	0.50	0.67	0.80

### Effect of Temperature.—

TABLE 100.  
0.50*n* metol in 0.02*n* NaOH at 10°.

Time in minutes ...		1.0.	2.0.
No.	Log E.	D <sub>1</sub> .	D <sub>2</sub> .
1	1.00	0.020	0.072
2	1.36	0.084	0.145
3	1.575	0.158	0.326
4	1.80	0.270	0.479
5	2.14	0.410	0.686
6	2.42	0.547	0.896
7	2.72	0.680	1.124
8	3.01	0.816	1.305
9	3.30	0.970	1.570
	γ =	0.45	0.72

Comparison with rodinal showed that there was little difference in the velocity; thus with p-aminophenol at the same concentration the velocity was as follows :—

Metol .	$t$	0.5	1.0	1.5	2.0	$\infty$
	$\gamma$	0.40	0.50	0.67	0.80	2.50
Rodinal	$t$	0.5	1.0	1.5	—	$\infty$
	$\gamma$	0.42	0.61	0.70	—	2.50

Hence  $K_{\text{metol}} = 0.53$ .

The temperature-coefficient is very small; at  $10^\circ$   $\gamma.5$  time = 1.25, at  $20^\circ$  1.00. Hence  $\frac{K + 10^\circ}{K} = 1.25$ .

### Affinity, Reduction Potential, and Bromide Sensitiveness.

—Even if the velocity of development were simply that of the chemical oxidation process, it would be no measure of the affinity of the reducer, though possessing more value as a characteristic constant. But the velocity in heterogeneous reactions depends so much upon diffusion processes that its value is very slight as a coefficient of affinity.

As Abegg<sup>1</sup> has pointed out, the process of development, which may be generally symbolised by the equation  $R'' + Ag \rightleftharpoons R' + Ag$ , can be divided into the two simultaneous processes,  $R'' \rightarrow R'$  and  $Ag \rightarrow Ag$  (metal), related to each other by the stoichiometric laws, and each tending to its natural equilibrium represented by a definite value of the ratios  $\frac{R''}{[R']}$  and  $\frac{[Ag']}{[Ag]}$ . For the reaction  $R'' + Ag \rightleftharpoons R' + Ag$  we have at equilibrium  $[R''] [Ag] = K [R'] [Ag]$  (see p. 93), when the free energy of the reaction is given by the expression—

$$F = RT \log \frac{[R''] [Ag]}{[R'] [Ag]}$$

Separating the components, the potential of an ion  $R''$ , which passes to a higher oxidation stage,  $R'$ , is of the form  $A = RT \log \frac{[R'']}{[R']}$ ; the electro-motive force in a chain, which is proportional to this, by the expression<sup>2</sup>—

$$E = a + \frac{RT}{c} \log \frac{[R'']}{[R']}$$

<sup>1</sup> *Eder's Jahrbuch*, 1904, 1-5.

<sup>2</sup> Peters, *Zeit. phys. Chem.*, 1898, 26. 193; Fredenhagen, *Zeit. anorg. Chem.*, 1902, 29. 396; Luther, *Zeit. phys. Chem.*, 1901, 36. 397.

If the value  $\frac{[R'']}{[R']}$  will not naturally reach a limit forcing  $\frac{[Ag']}{[Ag]}$  past a certain value such that metallic silver is precipitated, the reducer is too weak to act as a developer. Since  $[Ag]$  is constant for the same exposure (see p. 112), this minimum value of  $[Ag']/[Ag]$  depends for this only on  $[Ag']$ , and the maximum in the absence of free halide ions is fixed for any specific halide by its solubility-product. Obviously a reducer of greater reduction potential is required for silver bromide than for silver chloride, while the reduction potential of the developer must be increased as the concentration of bromide ions is increased, since  $[Ag'][Br'] = \text{constant}$ .

**Dependence of Reduction Potential on Concentration and Alkali.**—The reducing agent being in general the anion of a weak acid, it follows from the equation  $R' + H_2O \rightleftharpoons RH + OH'$ , and the application of the mass law  $[R'] = K[RH][OH']$ , that increase both in the concentration of the reducer and of the alkali will in general increase the reduction potential. But this effect is complicated by certain side reactions, whereby the alkali further augments the potential, while the reducer diminishes it.

From the foregoing it is obvious that the addition of the primary oxidation product should lower the reduction potential of the developer and the free energy of the reaction. Whilst this is found true for ferrous oxalate, with organic developers there are complications. The oxidation product is not generally stable under the conditions of the solution, being frequently reconverted by a side reaction to the reducer (see p. 152). The alkali, by removing the oxidation product, increases the reduction potential. If, then, the reducer be in such excess as to greatly lower the concentration of the free hydroxyl ions, it may in this way diminish the effective potential, while it may further decrease the energy of the reaction by forming complex ions with the silver ion (see p. 138); both these causes offer an explanation of the retarded action frequently noticed with excess of reducer.<sup>1</sup> In the case of the inorganic bodies

<sup>1</sup> Compare quinol, Chap. V. p. 169; and for pyrogallol, Hurter and Driffield, *Phot. Journ.*, 1898.

$\text{NH}_2\text{OH}$  and  $\text{H}_2\text{O}_2$ , the oxidation products are gases which are removed as soon as the solution reaches a certain degree of supersaturation. That the action is essentially reversible, and that the gases in solution possess a certain oxidation potential, appears probable from the fact that bromide exerts a retarding action on the lower tones.

From these considerations it will be seen that the attempt to determine electrically the reduction potentials of organic reducers can give no reliable results, and, in fact, measurements of the E.M.F.'s with either silver electrodes coated with silver bromide in potassium bromide,<sup>1</sup> or with oxygen-charged Pt. electrodes, gave only inconstant and varying values. In agreement with Fredenhagen,<sup>2</sup> the potential of a reducing agent is indeterminate, unless a definite concentration of the oxidation product be present. As explained, the addition to organic developers of the oxidation product has no effect in retarding development. Abegg proposed to characterise the reducing energy of the developers by the concentration of bromide which they could just overcome and start development (cf. p. 94). But while this method can be used with ferrous oxalate, where the concentration of the oxidation product is determinate, it fails with organic reducers for the reasons given. With these the reducing energy depends upon the stability of the oxidation products; when formed, these exert their reversing action, but they disappear in time, so that the energy is a function of the time. For these reasons it appeared that a dynamical method, if possible, would give a truer practical measure of the energy of the reducer, this being a function of its *natural* potential as defined above and of the time of existence or life of its oxidation product. The method employed was to compare the depressions in density produced by bromide. The general phenomena of the retarding action has been dealt with in a previous section. It was shown that over a certain range of exposure bromide produces for the same time of development an equal or constant depression of density, or generally the exposure curve is referred to as

<sup>1</sup> Jahn, *Zeit. phys. Chem.*, 1900, **33**, 555.

<sup>2</sup> *Zeit. anorg. Chemie*, 1902, **29**, 396.

a new origin. The shift was found to be, with ferrous oxalate, directly proportional to the concentration of bromide, and inversely proportional to the time of development. Hence, knowing the development constants  $K$  and  $\gamma_{\infty}$  for a given plate, and also knowing the depression produced by bromide at a given degree of development ( $\gamma$ ) for a given concentration, then the depression for any other degree or concentration, within limits, may be calculated. By this means, if the depression with other developers be measured, then the concentration of bromide necessary to produce with ferrous oxalate the *same* depression at the *same* degree of development can be calculated, and hence a numerical measure of the reducing energy of the developer compared with that of ferrous oxalate. In this way the following data were obtained for ferrous oxalate, hydroxylamine, quinol, and p-aminophenol :—

TABLE 101.

Ferrous oxalate, series A of plates. Densities for 3'0 minutes in no bromide and  $n/100$  Br'.

No.	Log E.	$D_0$ .	$D_{Br}$ .	$\Delta D$ .
1	1'00	0'040	—	0'040
2	1'36	0'080	0'015	0'065
3	1'575	0'175	0'040	0'135
4	1'80	0'326	0'110	0'216
5	2'14	0'520	0'238	0'282
6	2'42	0'722	0'420	0'302
7	2'72	0'930	0'618	0'312
8	3'01	1'099	0'833	0'266
9	3'30	1'312	1'032	0'280
Mean =				0'288

From the curves,  $\gamma = 0'645$

hence  $\Delta D = \gamma (\log i_{Br} - \log i)$

$= 0'645 (1'75 - 1'30)$

$= 0'290$ .

For the same plate, with hydroxylamine, for 3 minutes in 0.10*n* NH<sub>2</sub>OH,  
in 0.047*n* NaOH, in *n*/200 and *n*/400 KBr.

No.	Log E.	D <sub>0</sub> .	D <sub>1</sub> .	D <sub>2</sub> .	ΔD for <i>n</i> /200.
1	1.00	0.056	—	—	—
2	1.36	0.116	0.060	0.080	0.056
3	1.575	0.203	0.140	0.164	0.060
4	1.80	0.355	0.243	0.301	0.112
5	2.14	0.560	0.446	0.504	0.114
6	2.42	0.760	0.625	0.701	0.135
7	2.72	0.932	0.801	0.878	0.131
8	3.01	1.140	1.011	1.091	0.129
9	3.30	1.340	1.207	1.263	0.133
Mean =					ΔD 0.128

$$\begin{aligned}
 \text{From the curves, } \Delta D &= \gamma (\log i_{\text{Br}} - \log i) \\
 &= 0.645 (1.45 - 1.25) \\
 &= 0.129.
 \end{aligned}$$

We have therefore with hydroxylamine a depression of 0.129 for *n*/200 bromide, and at the same  $\gamma$ , a depression of 0.290 for *n*/100 bromide with ferrous oxalate. Hence the concentration of bromide with hydroxylamine is 0.0113, to produce the same effect as 0.0100 with ferrous oxalate.

The measurements for quinol and rodinal were made with series B of plates; the development ( $\gamma, t$ ) curve with ferrous oxalate was as follows:—

TABLE 102.

*n*/10 ferrous oxalate at 20°.

<i>t</i> ...	2.0,	3.0,	5.0,	6.0,	∞
$\gamma$ ...	0.45,	0.74,	1.00,	1.17,	2.50
$\kappa$ ...	0.043,	0.050,	0.044,	0.046	

$$\text{Mean } K = 0.046.$$

The bromide depression for *n*/100 KBr for 3.0 minutes was—

No.	Log E.	D <sub>0</sub> .	D <sub>Br</sub> .	ΔD.
1	1.00	0.044	—	—
2	1.36	0.127	0.020	0.107
3	1.575	0.242	0.067	0.175
4	1.80	0.412	0.143	0.270
5	2.14	0.647	0.258	0.390
6	2.42	0.865	0.438	0.427
7	2.72	1.094	0.616	0.488
8	3.01	1.305	0.850	0.455
9	3.30	1.505	1.020	0.485
ΔD =				0.450

From the curves,  $\Delta D = \gamma (\log i_{Br} - \log i)$

$$= 0.74 (1.80 - 1.25)$$

$$= 0.410.$$

TABLE 103.

6.0 minutes in hydroquinone, 0.05*n* quinol in 0.05*n* NaOH and  
*n*/100 KBr.

No.	Log E.	D <sub>0</sub> .	D <sub>Br</sub> .	ΔD.
1	1.00	0.100	0.035	0.065
2	1.36	0.171	0.047	0.124
3	1.575	0.308	0.160	0.148
4	1.80	0.580	0.286	0.294
5	2.14	0.912	0.531	0.381
6	2.42	1.186	0.036	0.350
7	2.72	1.387	1.108	0.279
8	3.01	1.660	1.364	0.296
9	3.30	1.962	1.702	0.260
ΔD =				0.320

From the curves,  $\Delta D = \gamma (\log i_{Br} - \log i) = 0.97 (1.60 - 1.25)$

$$= 0.340 \text{ at } \gamma = 0.97.$$

And at  $\gamma 0.85$   $\Delta D = 0.85 (2.25 - 1.55).$

$$= 0.595 \text{ at } \gamma = 0.85.$$

TABLE 104.

P-aminophenol for 3.0 minutes, 0.05*n* NaOH and *n*/100 KBr.

No.	Log E.	D <sub>0</sub> .	D <sub>Br</sub> *	ΔD.
1	1.00	0.055	0.035	0.020
2	1.36	0.144	0.104	0.040
3	1.575	0.268	0.187	0.081
4	1.80	0.401	0.308	0.093
5	2.14	0.594	0.481	0.113
6	2.42	0.796	0.661	0.135
7	2.72	0.975	0.876	0.100
8	3.01	1.152	1.020	0.132
9	3.30	1.323	1.163	0.160
ΔD =				0.128

\* From the curves,  $\Delta D = \gamma (\log i_{Br} - \log i)$   
 $= 0.64 (1.40 - 1.20)$   
 $= 0.128.$

Collecting the results, we have—

Series A.— $\Delta D$  for  $\text{FeC}_2\text{O}_4 = 0.290$  for 0.01*n* KBr at  $\gamma.645$ .

„  $\text{NH}_2\text{OH} = 0.129$  „ 0.005*n* „ „

K = 0.061.  $\gamma_\infty = 2.18.$

Series B.— $\Delta D$  for  $\text{FeC}_2\text{O}_4 = 0.410$  for 0.01*n* KBr at  $\gamma.74$

„  $\text{C}_6\text{H}_4(\text{OH})_2 = 0.340$  „ „ „  $\gamma.97$

„ „ = 0.595 „ „ „  $\gamma.85$

„  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{OH} \\ \diagup \\ \text{NH}_2 \end{smallmatrix} = 0.128$  „ „ „  $\gamma.64$

K = 0.046.  $\gamma_\infty = 2.50.$

Now, for ferrous oxalate  $\Delta D = \frac{a[\text{Br}]}{t}$ , where [Br = conc. of bromide,  $t$  = time of development, and  $a$  is a constant; while, since  $t = \frac{\log \gamma_\infty - \log (\gamma_\infty - \gamma)}{K}$ , the depression can be calculated for each value of  $\gamma$  for ferrous oxalate, and then the value of [Br found, which produces the *same* depression at this  $\gamma$  as with the reducer in question. In this way the following table was obtained from the foregoing data:—

Concentrations of bromide required to produce the same depression as 0.01*n* KBr with ferrous oxalate—



$\text{FeC}_2\text{O}_4$ , 0.01*n*.

$\text{NH}_2\text{OH}$ , 0.0113*n*.

$\text{C}_6\text{H}_4(\text{OH})_2$ , 0.0052*n* at 34 per cent. development.  
0.0070*n* at 40 per cent. „

$\text{C}_6\text{H}_4\text{OH.NH}_2$ , 0.034*n*.

These numbers may be taken as expressing the relative reducing energies of the developers compared with ferrous oxalate. It will be seen that p-aminophenol is much the most energetic of those tried; next comes hydroxylamine, while hydroquinone has only one-half to two-thirds the energy of ferrous oxalate.

The results for alkaline development may be numerically tabulated under the following terminology:—

K = velocity of development per gram-molecule at 20°

$$= \frac{1}{t} \log_{10} (\gamma_x / \gamma_x - \gamma).$$

E = efficiency, *i.e.* velocity of development compared with ferrous oxalate at 20°, divided by R.

R = reducing power, *i.e.* gram-molecules of AgBr reduced by one gram-molecule of reducer.

T.C. = temperature-coefficient =  $\frac{K + 10^\circ}{K}$ .

F = energy = concentration of bromide producing same retardation as with ferrous oxalate for 0.01*n* KBr.

### Summary.

Developer.	R.	K.	E.	T.C.	F.
Ferrous oxalate. $\text{Fe}(\text{C}_2\text{O}_4)_2$	1	0.061	1.00	1.70	0.01 <i>n</i> = 1.00
Hydroxylamine. $\text{NH}_2\text{O}'$	1	0.305	5.0	2.10	0.0113 <i>n</i> = 1.13
Quinol. $\text{C}_6\text{H}_4\text{O}_2$	2	0.146	1.20	2.80	0.0052 <i>n</i> = 0.52 0.0073 <i>n</i> = 0.73
Hydrogen peroxide. $\text{O}_2\text{H}'$	1	—	—	—	—
P-aminophenol. $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{O}' \\ \text{NH}' \end{smallmatrix}$	(2)	0.550	4.5	1.50	0.034 <i>n</i> = 3.4
Metol. $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{O}' \\ \text{NCH}_3' \end{smallmatrix}$	(2)	0.500	4.4	1.25	—

We have seen from above that if the reduction potential for given reactivity of halide be sufficient to form a silver germ, then the value of  $\log i$  reaches ultimately a normal value. This question has an important bearing on sensitometry, since the statement is frequently made that the speed of the plate, *i.e.* the reciprocal of the inertia, varies with the developer. A special investigation showed that two groups of plates exist. For one the ferrous oxalate inertia is the same as for organic developers, the differences among these being but slight. For the other the ferrous oxalate inertia is 1.74 times that given by organic reducers. But as there is no regression of the inertia, this does not seem to have much to do with the potential of the reducer. Further investigation showed that in a plate of the first type a slight fuming with ammonia was sufficient to increase the ferrous oxalate inertia, so that the phenomenon appears to be associated with the nature of the latent image, and will be mentioned again. So far as *normal* development is concerned, the developers with different energy show but little difference in the inertia or speed of the plate. But some slight difference there is, as the following figures, which give the maximum and minimum values of  $\log i$ , obtained without bromide out of the series investigated for alkaline development:—

Developer.	$\log i_{\max.}$	$\log i_{\min.}$
Ferrous oxalate . . . . .	1.25	1.30
Hydroxylamine . . . . .	1.20	1.25
Quinol . . . . .	1.20	1.55
Rodinal . . . . .	1.15	1.10
Metol . . . . .	1.15	—

It has already been mentioned that the presence of very little alkali compared with reducer, besides great dilution, may retard development with organic reducers, so that this must be borne in mind in considering the above figures. But the general trend indicates that the energy or potential of the reducer can certainly exercise some effect on the speed of the plate even with maximum development.

## CHAPTER VI

### THE NATURE OF THE DEVELOPABLE CONDITION—THE LATENT IMAGE

So far the nature of the "latent image" has only been incidentally touched upon. In the previous chapters on the chemical dynamics of development, it was only assumed that we could postulate a difference between exposed "developable" halide and the unexposed "undevelopable" halide, the mass of the former being only determined by the exposure, while the amount of the latter reduced during the total time of development was negligibly small. This working hypothesis was not contradicted by the dynamics of normal development, and accounted for the law of constant density-ratios. But the microscopic inquiry, the investigation of reversibility and of the action of alkaline reducers with different potentials from ferrous oxalate, showed that the "developable" halide differed in degree rather than absolutely, and that not only the mass of developable halide was determined by the exposure, but also a certain reactivity which was made more evident by retarded development. The essential of this reactivity appeared to lie rather in the starting of development by curtailing an induction period than in a change of the *rate* of reduction.

Before proceeding further with this line of argument, it may be well to briefly discuss some of the theories hitherto advanced as to the nature of the latent image and its function in development. To do so with anything like completeness would demand more space than is either desirable or necessary, since the amount of speculation has been quite disproportionately great compared with the experimental evidence of real value.

The uncertainty as to the nature of the visible blackening of silver salts in light—the reaction product being variously considered as silver, subchloride, oxychloride, or mixtures of these—has been even more apparent with regard to the invisible change rendered apparent by development. The developable condition in a halide emulsion may be effected by a large number of agencies, which may for the present be grouped as follows<sup>1</sup>:—

- (a) Ether vibrations, from the infra-red to the ultra-violet.
- (b) Röntgen-rays, Kathode-rays, Becquerel-rays ( $\beta$  and  $\gamma$  radiations from the radio-active bodies).
- (c) Mechanical stress or pressure.
- (d) Chemical action.
- (e) Heat.

This varied causation will be referred to again, but meanwhile it may be noted that K. Schaum,<sup>2</sup> in an attempt to systematise the chemical actions (*d*) on photo-films, has pointed out the importance of some decision as to pure chemical action in view of the frequent and increasing use of the photographic plate as an indicator of radio-activity. Considering only the change produced by light, there are, and always have been, two sets of theories as to its nature, the one considering it purely physical, the other postulating a chemical change. We shall briefly refer to the main theories of both groups, and then, in a short attempt to systematise the principal experimental evidence, including our own, consider how far any of these are borne out.

The chemical theories fall into two groups, following the division of opinion as to the visible image:—

- (a) Reduction to silver or subhalide.

Subhalide	{	Abney, <i>Instruct. in Phot.</i> , 11th edit., Ch. I.
		J. M. Eder, <i>Ausf. Handb.</i> , II., 2 Aufl. III.
		Carey Lea, <i>Silliman's American Journ.</i> (3), 33. 343.
		Luther, <i>Zeit. phys. Chem.</i> , 1899, 30. 628.
Silver: Abegg, <i>Phot. Korr.</i> , 1899, 276; <i>Arch. wiss. Phot.</i> , 1899, I. 268.		

<sup>1</sup> Cf. C. Lea, *Phil. Mag.*, 1891, 320.

<sup>2</sup> *Zeit. wiss. Phot.*, 1904, II. 205.

(b) Oxidation to oxychloride.

Meldola, *Chemistry of Phot.*, 1891, 53 *et seq.*

Tugolessow, *Phot. Corr.*, 1903, 594.

W. Braun, *Zeit. wiss. Phot.*, 1904, II. 290.

The subhalide theory assumes that the visible and invisible image consists of a lower halide, generally attributed the formula  $\text{Ag}_2\text{Br}$  (Abney, Lea, Luther), while others (Eder), with little opinion of the laws of simple proportion and valency, assign to it a Protean constitution, represented by  $\text{Ag}_x\text{Br}_{x-y}$ , varying the same to suit special requirements. Others, again, suggest that the subsalt forms homogeneous mixtures or solid solutions with unaltered halide.<sup>1</sup> The existence of definite subhalides of silver has long been a matter of dispute. While Gunz's subfluoride<sup>2</sup>  $\text{Ag}_2\text{F}$  appears to comply with the tests for a definite chemical individual, other so-called subhalides,<sup>3</sup> on examination, behave quite as mixtures of normal halide and silver.<sup>4</sup> That the synthetic subhalides are certainly unstable products appears from their great reactivity.<sup>5</sup> The best evidence in favour of their existence is due to the electrical work of Luther<sup>6</sup> and Baur (*loc. cit.*), from which it appears most probable that their formula is  $\text{Ag}_2\text{X}$ , forming, however, solid solutions in all proportions with  $\text{AgX}$ . The nature of the evidence and further development of the subhalide theory are considered later.

The silver or silver germ theory was indicated by Ostwald,<sup>7</sup> and then strongly brought forward by Abegg.<sup>8</sup> Proceeding from the fact that a "germ" of metallic silver will induce the deposition of further silver upon it from a supersaturated solution, it provides the most satisfactory theory of development, but fails to account for the resistance of "latent image" to oxidising solutions of such potential as to destroy metallic silver. It is

<sup>1</sup> Lea, *loc. cit.*; Baur, *Zeit. phys. Chem.*, **45**. 618; Günther, *Abh. d. naturh. Ges. Nürnberg*, 1904, 15.

<sup>2</sup> *Comptes Rend.*, **112**. 861, 1212.

<sup>3</sup> O. Vogel, *Phot. Mit.*, **36**. 334.

<sup>4</sup> K. Emszt, *Zeit. anorg. Chem.*, **28**. 346.

<sup>5</sup> Gunz, *Rev. des sciences Phot.*, 1905, 304.

<sup>6</sup> *Zeit. phys. Chem.*, 1899, **30**. 680.

<sup>7</sup> *Allgem. Chemie*, 3<sup>te</sup> Auflage, **II**. 1078.

<sup>8</sup> *Arch. wiss. Phot.*, 1899, **I**. 268.

also to some extent inconsistent with the initial induction in development. The oxyhalide theory, proposed by Meldola, and supported by some experiments of Brereton Baker (for the visible image), considers that the photographic image is due to photo-oxidation, oxyhalides of the type  $\text{Ag}_4\text{OX}_2$  being formed. Although Braun (*loc. cit.*) finds that the latent image is stronger when the oxygen concentration is high, this action appears to be due to some side reaction, since both the invisible change and the visible blackening can take place either *in vacuo*, in solvents free from oxygen, or in the presence of reducing agents, precluding free oxygen. The influence of moisture in the photographic reaction is a moot point, and will be referred to later, as also the part played by oxygen.

Various objections to any chemical change have induced many workers to favour—at any rate for slight exposures—a purely physical or so-styled molecular alteration. Before mentioning any of the special physical theories, the criticism directed against the chemical theory should be mentioned, and a possible reply to the same. A fair statement of the case against a chemical change will be found in Mr. Chapman Jones's *Science and Practice of Photography*, 1904.

*Objection.*—That the energy supplied by light is not sufficient to dissociate the total mass of halide developed, nor is there any evidence of an appreciable quantity of halogen being released.<sup>1</sup>

*Reply.*—That the change is limited to a very small and quite unweighable quantity of the halide, which then induces the reduction of the rest.

*Objection.*—That in that case the reduction should extend to the whole mass of halide, whereas a maximum is reached for each exposure.

*Reply.*—That the halide *grain* is the unit in development, so that only the grains with a sufficient nucleus of the photo-product develop.

*Objection.*—That the existence of this minute proportion of the admittedly unstable photo-product is inconsistent with the stability of the latent image under many conditions and over long periods of time.

<sup>1</sup> Hurter and Driffeld, *Phot. Journ.*, 1898, 22. 149.

*Reply.*—That the latent image *does* tend to disappear in time, especially under unfavourable chemical conditions, while it can be destroyed by oxidising solutions. Further, that a minute quantity of one body forming a solid solution with another body of similar constitution has a much greater stability than the same substance in mass.

*Objection.*—That reversal brought about by long exposure is inconsistent with the application of the mass law to the process, whereby only a neutral state of no further change should be reached.

*Reply.*—That reversal can by certain modifications of exposure and development be retarded or nearly annulled, and may be plausibly shown to be partly due to an after effect in development, partly to the peculiar nature of photo-chemical equilibria.

Finally, it is maintained that the onus of proof rests with those who suggest a chemical change, that a physical or molecular modification must precede the chemical dissociation; which change is sufficient to account for the altered properties of the halides. To this it may be replied that the action of oxidising agents on the latent image and the existence of an image capable of physical development after fixation are difficult or impossible to explain on the physical theory or any but that of chemical reduction; while the various specific physical theories proposed are either inadequate to the facts or vague molecular hypotheses incapable of disproof.

The more important are now cited. Lagermac<sup>1</sup> suggested that light caused a crystallisation of the halide, but it is not stated how this would facilitate reduction. Bredig<sup>2</sup> put forward a "zerstaubungs theorie," the halide in light breaking up into smaller particles, whose increased solubility facilitated reduction. Hurter and Driffeld thought that light might depolymerise complex  $(AgX)_m$  molecules.

Analogy with elastic phenomena has suggested to many observers the ideal of a "strain" in the halide. In particular J. C. Bose<sup>3</sup> has brought forward a "molecular strain" hypothesis

<sup>1</sup> *Brit. Journ. Phot.*, 1897, 94.

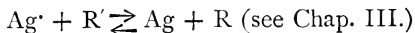
<sup>2</sup> *Arch. wiss. Phot.*, 1899, I. 46; *Eder's Jahrbuch*, 1899, 363.

<sup>3</sup> *Proc. Roy. Soc.*, 1902; *Phot. Journ.*, 1902, 26. 146.

in explanation of the changes of conductivity, E.M.F., and surface tension of surfaces exposed to stimulus—mechanical stress or pressure, light, Hertzian waves, etc. It is maintained with regard to the photographic process that it gives a simple explanation of various obscure phenomena of photographic action, such as the relapse of the latent image, recurrent and abnormal reversals, and dependence of the photo-effect on the time-rate of illumination.

This is not the place to criticise in detail Professor Bose's theory of "molecular strain" in its applications to coherer action, response to stimulus, etc., but, as bearing on photography, we may suggest that there is a suspicion of a vicious circle in the argument. The elastic behaviour of matter in bulk is transferred to the molecules, whereas a consistent molecular theory should surely afford an explanation of elastic phenomena themselves. Generally it may be said of the physical theories that they shirk a real explanation by treating the phenomenon to be explained as a quality of the physical modification of the halide, much as the narcotic power of opium was attributed by mediæval mediciners to a "somniferous principle" peculiar to the drug. Meantime the primary fact requiring explanation seems to be somewhat neglected—namely, the acceleration of reduction by the developer.

**The Developable Condition in Silver Halides.**—The chemical action in development has already been dealt with, reduction of silver ions to metallic silver, typified by—



How may this action be accelerated or retarded, and in particular, catalysed, as by the latent image? The key to this appears to lie in the reversibility of the reaction and the silver-germ theory of development. In the absence of metallic silver the reaction may reach two possible conclusions—

- (a) equilibrium is reached before metallic silver is precipitated.
- (b) silver is precipitated and the rate of the reverse reaction lowered; reduction proceeds till the grain is exhausted.

Let us consider quite generally the phenomena of reduction with silver bromide, free and emulsified.



**Non-emulsified Silver Halides.**—The behaviour of these has been investigated by Luther<sup>1</sup> and K. Schaum and W. Braun.<sup>2</sup> We prepared our plates in a somewhat similar manner to these investigators, as follows: very carefully cleaned matt-glass strips ( $4\frac{1}{4} \times 1\frac{1}{4}$  ins.) were levelled by laying them on mercury in a large vessel; this was filled with 500 c.c. of a dilute solution of HBr, and there was added through a narrowed opening of a glass tube, which itself acted as stirrer, about 100 c.c. of 5 per cent. AgNO<sub>3</sub>. The fine suspension took some three days to settle. The plates were removed, dried at air-temperature in the drying cupboard, and then carefully washed by standing in distilled water, repeatedly removed by the pump. On final drying a fairly coherent even film was obtained.

**Action of Developers.**—In agreement with Schaum and Luther, and in opposition to Lüppo-Kramer, we find that exposure to light accelerates the initial reduction by the developer, although, unless a somewhat restrained solution be used, the distinction between exposed and unexposed bromide is soon lost. If the bromide be suspended in gelatin, the reduction without exposure is much retarded, while the bromide removed from a rapid emulsion is much quicker to start reduction without exposure than freshly precipitated bromide. These facts lead us to agree with Abney and Schaum, that the gelatin, mechanically or chemically, retards reduction, Lüppo-Kramer's conception that emulsification brings about "enormous and absolute modifications" in the silver bromide being quite unjustified. Schaum points out that the idea of various allotropic forms of precipitated halides is untenable, the only forms being amorphous and crystalline.

Of an amorphous body but one modification is possible; thus the various forms of silver halides distinguished by Stas<sup>3</sup> differ only in their degree of division and content of foreign substances. The formation of solid solutions by the amorphous halide and its effect on the photo-chemical behaviour is discussed later. Passing next to emulsified halides, if a

<sup>1</sup> *Zeit. phys. Chem.*, 1899, **30**, 628.

<sup>2</sup> *Zeit. wiss. Phot.*, 1904, **I**, 377.

<sup>3</sup> *Annal de Chim. et Phys.*, 1874, 289.

dry plate (slow) of the type used for the experimental work of this thesis be treated with a developer, *without previous exposure to light*, the following phenomena are observed :—

(a) With ferrous oxalate, slightly acid, the plate may remain some twelve or more hours in the developer without a greater density than 0.2 being formed. Continued treatment increases the fog, which can generally be divided into two parts. One consists of small discrete particles similar to those on development of exposed halide. But also, and chiefly on the surface, dichroic fog is formed, a silver deposit of varying tone, very finely divided, and showing complementary colours by reflected and transmitted light.<sup>1</sup> If the ferrous oxalate developer be rendered *alkaline*, the fog is greatly increased, but the rate of development unaltered. The increased fog is probably due to slight formation of ferrous hydrate (see (d), later).

*With fast plates* or highly ripened emulsions the black fog starts early, attaining a maximum similar to a mean exposure ; there is generally more dichroic fog.

(b) With alkaline development, defect of alkali, the phenomena are similar to those with ferrous oxalate, but more intense, though the plate never seems to be completely reduced.

(c) With excess of alkali nearly complete reduction may be obtained in time.

(d) With certain reducers of very high potential, such as alkaline ferrous hydrate, stannous chloride, triamidophenol, and pyrogallol, with excess of caustic alkali, there is a rapid and complete reduction of the silver bromide, without exposure.

(e) Insolation or exposure to light, etc. The phenomena have already been described. If a latent image be formed by Röntgen rays, etc., the development takes place in a manner similar to that of the light-exposed halide. The following three series give values for the density obtained on development for—

(a) 60 C.M.S.

(β) Exposure to 20 per cent. hydrogen peroxide for 8 hours.

(γ) Exposure to thoria powder for 7 days.

The developer was  $n/10$  ferrous oxalate at 20°.

<sup>1</sup> Cf. Lumière and Seyewetz, *Phot. Journ.*, 1903, 53. 226.

TABLE 105.

(a) 60 C.M.S. (β) H<sub>2</sub>O<sub>2</sub>. (γ) thoria.

<i>t</i> in minutes.	D <sub>α</sub> .	D <sub>β</sub> .	D <sub>γ</sub> .
2·0	0·520	0·324	0·219
4·0	0·609	0·578	0·392
6·0	0·807	0·783	0·503
10·0	1·108	1·061	0·705
20·0	1·461	1·403	0·930
120·0	1·628	1·542	1·036
∞	1·624	1·561	1·032

These three series all agree with the exponential formula  $K = 1/t \log D_{\infty}/D_{\infty} - D$ , and give the same value,  $K = 0·050$ , for the rate of development. The *rate of development is the same*, however the developability is brought about.

The reaction  $Ag \cdot + R'' \rightleftharpoons Ag + R'$  reaches an equilibrium defined by  $[Ag \cdot][R''] = K[Ag][R']$ . In the absence of metallic silver or any cause facilitating its deposition, the concentration of metallic silver must reach a metastable limit before precipitation. The experimental evidence in favour of Ostwald's conception of a metastable limit for supersaturated solutions has been increased by the investigation of Liesegang's rings. S. Liesegang<sup>1</sup> found that on adding to a thin gelatin film soaked with silver nitrate a drop of potassium chromate, that the silver chromate was precipitated in rings, each lying further from the centre and separated by a blank space. The same formation may be obtained in tubes, laminae at right angles to the axis being formed. Ostwald suggested that this was a supersaturation phenomenon, bearing out his theory of a metastable limit. Morse and Pierce<sup>2</sup> investigated the matter further; they showed that many substances showed similar behaviour under like conditions, gases also being evolved in layers. For silver chromate they made quantitative measurements,

<sup>1</sup> *Ueber Chem. Reaktionen in Gallerten*, Düsseldorf, 1898.<sup>2</sup> *Zeit. phys. Chem.*, 1904, **45**. 600.

and showed that in the absence of solid chromate the product  $[Ag^+ \times [CrO_4]^-]$  reaches a constant value,  $M$ , analogous to the solubility product, but representing a concentration of  $Ag_2CrO_4$  some 150 times that in presence of the solid chromate.

We made some qualitative experiments to see if Liesegang's rings could be made with metallic silver.

(1) 5 per cent. gelatin, 3 per cent. ammoniacal  $AgNO_3$  was solidified in tubes, and these dipped in 1/200 and 1/100 molar pyrogallol. Beside a nearly general formation of coloured silver (red to purple), definite layers of black or brown silver were formed.

(2) 5 per cent. gelatin with 3 per cent.  $AgNO_3$ , dipped in  $n/100$ ,  $n/50$  solutions of ferrous fluoride. Less dichroic silver, but again definite layers of silver.

From this we conclude that by reduction from the ionic state the metallic silver formed either ( $\alpha$ ) reaches a metastable limit and is precipitated as solid metal, or ( $\beta$ ) forms a colloidal solution, which may be coagulated by electrolytes. Hence in a gelatino-bromide plate any "germ" tending to the deposition of metallic silver below the metastable limit can give rise to the so-called developable condition. While the most favourable "germ" is that of the solid substance itself, it appears from the behaviour of supersaturated solutions that "germs" of unknown constitution are also more or less effective. Thus G. Jaffe,<sup>1</sup> in some studies on supersaturation, using  $KNO_3$  at constant temperature and also surcooling, found that by repeated filtration the "life" of a solution could be greatly prolonged; while three filtrations had but little effect, with 7 to 12 the average life was prolonged from 15 to 27 hours, in some cases to 12 days. His chief conclusions were—

(1) By mechanical purification the metastable limit can be raised under all conditions; germs are removable by filtration.

(2) If the precipitate can exist in more than one modification, the unstable appears first.

This investigation appears to throw considerable light on the function of gelatin in retarding development (*vide* p. 203).

<sup>1</sup> *Zeit. phys. Chem.*, 1903, **43**, 565.

Not by alteration of diffusion, but by filtration of "germs" which lower the metastable limit, does gelatin act as a protective sheath to the silver halide. In part also it forms solid solutions with the AgBr, beside complex ions with the silver ion, all causes tending to increase the stability of the silver salt against reduction. This protective influence of gelatin explains to some extent why the destruction of it by alkalis, acids, and oxidising solutions renders a plate developable. [Note.—The action of oxidising agents is not entirely explained by this, as a similar action is found with plain silver bromide (Schaum and Braun, *loc. cit.*) and with collodion emulsions.<sup>1</sup>]

We see now that the developable condition is in general due to a lowering of the metastable limit of the silver solution. A silver germ is then formed, and, with a reducer above a certain potential reduction, proceeds to the limit. The catalysis of reduction, which is termed development, may be considered as belonging to the first class of Ostwald's scheme.<sup>2</sup> The peculiarities of various latent images are due to the diversity of the "germs" acting as Boden-Körper. Efficient are—

(a) Foremost, *silver germs*. Experiments on the inducement of development by introducing metallic silver into gelatin emulsions have not always given satisfactory agreement.<sup>3</sup> Abegg and Herzog<sup>4</sup> found that the addition of finely divided silver somewhat increased the reducibility. Lüppo-Kramer<sup>5</sup> found that "grainless" silver from a Lippman emulsion made a collodion emulsion completely reducible, but had no action with a gelatine emulsion. Here the protective influence of gelatine against "germs" appears to be in operation, which may also account for the uncertainty in repetitions of the well-known Abney effect.<sup>6</sup> To test this, we tried colloidal silver, prepared according to Carey Lea's method. The plate was soaked in a 10 per cent. solution of AgNO<sub>3</sub>,

<sup>1</sup> Eder, *Zeit. wiss. Phot.*, 1905, III. 339.

<sup>2</sup> *Über Katalyse*, Leipzig, 1902; *Zeit. Elektrochem.*, 1901, 7. 995.

<sup>3</sup> Cf. Precht, *Arch. wiss. Phot.*, II. 1900, 155.

<sup>4</sup> *Arch. wiss. Phot.*, I. 1899, 115.

<sup>5</sup> *Wiss. Arb.*, 33.

<sup>6</sup> Abney, *Phil. Mag.* (5), III. 46; Bredig, *Eder's Jahrbuch*, 1901.

and then treated with the following solution: 20 c.c. of 30 per cent. ferrous sulphate + 28 c.c. of 40 per cent. sodium citrate, to which was added 10 per cent. NaOH till the precipitate formed just dissolved. The solution and sludge on the surface were removed and the plate treated, after washing, with dilute HCl, which converts the colloidal silver into metallic. On adding a developer, there was considerable reduction, the amount appearing to depend somewhat on the first bath with  $\text{AgNO}_3$ . All the phenomena of development agree with the view that, a silver nucleus once formed, complete reduction of the grain is ensured.

(b) Reducer of very high potential. The silver is rapidly forced over the metastable limit and a silver germ formed (*vide* p. 204).

(c) Destruction of gelatin, already noted.

(d) Silver sulphide (see Chap. IV.).

(e) Other metals besides silver may act as "germs" for development.<sup>1</sup> While various metals, not incorporated with the emulsion, as in Baekeland's observations, can yet by mere contact with the film, or separated by paper, produce a developable impression, this effect is of uncertain mechanism, and is limited to the metals of higher decomposition tension than silver, *i.e.* less noble.<sup>2</sup> The action of gold and platinum precipitated in the film has not been described before.<sup>3</sup> If a gelatino-bromide plate be treated with a solution of auric chloride,  $m/100 \text{ AuCl}_3$ , for, say, six hours, the gold solution is slightly reduced by the gelatin, metallic gold being precipitated in the film. On treatment with  $n/10$  ferrous oxalate, the whole film was rapidly and completely reduced. Similar results were obtained with platinum. Gold and platinum being "nobler" metals than silver, there can in this case be no electrolytic action whereby a silver "germ" is formed (*cf.* Baekeland, *loc. cit.*), but the gold or platinum must itself function as development-germ.

<sup>1</sup> See Baekeland, *Zeit. wiss. Phot.*, 1904, I. 419.

<sup>2</sup> K. Schaum, *Zeit. wiss. Phot.*, 1905, II. 427.

<sup>3</sup> H. Weisz has recently published a paper describing this action. *Zeit. phys. Chem.*, 1906, 54. 305.

(*f*) Gas ions: the gases from flames are known to conduct electricity, attributed to ionisation.<sup>1</sup> While exposure of a dry plate to flame gases only gave uncertain results with subsequent development, a plate soaked in developer, whereof one half was shielded from the flame gases (Bunsen burner), showed by the fogging that the gas ions could form a nucleus for development.

(*g*) If a reducer of high potential be used in such small amount that there is no visible change, the plate becomes subsequently developable. Carey Lea showed that a trace of sodium hypophosphite produced a developable impression. Namias has found that alkaline stannous chloride acts similarly, which we have confirmed. No quantitative measurements have yet been made, and it is uncertain whether silver or subhalide is produced, but in any case the action may be considered as the initial stage of (*b*) above.

(*h*) Heat: with this is associated the fogging of over-ripened emulsions. A gelatin film tanned and then heated at about 100° fogs strongly on subsequent application of developer. That the gelatin exerts a reducing action at the high temperature seems probable.

(*i*) Exposure to radiant energy: with this action we shall now deal at slightly greater length. It is obvious that to conform to the theory adopted the light product must either itself function as the nucleus for reduction, *i.e.* itself lower the metastable limit, or by interaction with the developer furnish a silver germ. We have now to see what light the progress of the photo-chemical reaction throws on the nature of the product.

**Course of Reaction of Silver Halides in Light: the Plate-curve.**—In considering the rate of formation of the photo-bromide by light, the relation of this to the density of silver deposited—the only measure thereof—and of this latter to the exposure, are of primary importance. Of the many attempts, empirical and theoretical, to establish a relationship between the density on development and the exposure given, the best grounded still appears to be that of Hurter and Driffield.<sup>2</sup> This does not deal with the *nature* of the photo-product, but

<sup>1</sup> J. J. Thomson, *Conduction of Electricity in Gases*.

<sup>2</sup> *Journ. Soc. Chem. Ind.*, 1890, 9, 455.

simply assumes that the density on development is proportional to this, and then on the basis of certain assumptions obtains an expression for the amount of halide affected by light. The principle assumed is that the amount of halide affected at any moment is proportional to the mass of *unaltered* halide and to the light falling on this. The film is supposed to obey the exponential law for the absorption of light, and the rate of reaction is given by—

$$\frac{dx}{dt} = \frac{I}{\epsilon} (1 - a)(e^{-\kappa x} - e^{-\kappa a})$$

Here  $I$  is the original intensity of light,  $a$  the fraction reflected,  $\kappa$  the coefficient of absorption,  $x$  the changed and  $a$  the total halide, so that  $e^{-\kappa a}$  is the transparency, while  $\epsilon$  is the energy required to make  $dx$  developable.

Writing  $\rho$  for  $e^{\kappa a}$  and  $\beta = e^{\rho}$ , we have by integration—

$$D = \log_e (\rho - 1) \beta^{\kappa(1-a) \frac{It}{\epsilon}}$$

If we set  $\frac{\epsilon}{\kappa(1-a)} = i$ , and multiply by  $\gamma$ , to express the effect of development, we have for the density—

$$D = \gamma \log_e \left[ \rho - (\rho - 1) \beta^{\frac{It}{i}} \right]$$

The approximate form of this equation,  $D = \gamma \log E/i$ , has already been noticed. Under conditions of normal development, where the density-ratios are constant, the complete equation gives very fair agreement between the observed and calculated results; the curve which it represents for  $D$  plotted against  $\log E$  shows the first three periods of the characteristic curve:—

( $\alpha$ ) Under-exposure; flat and concave to axis of  $E$ ; here  $D = KE$ .

( $\beta$ ) Correct-exposure; nearly linear, *i.e.*  $D = K \log E$ .

( $\gamma$ ) Over-exposure and neutral period;  $D$  ceases to increase, so that  $D = K$ .

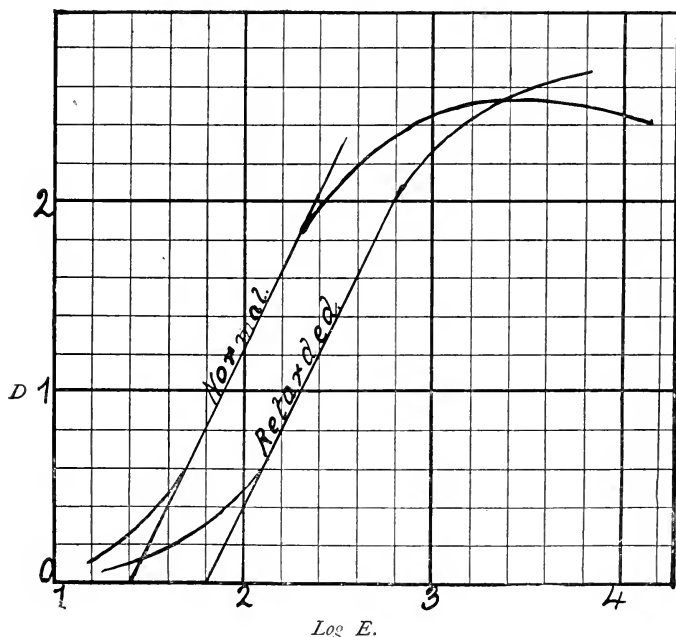
( $\delta$ ) Reversal;  $D$  decreases with increasing  $E$ . This speedily reaches a neutral stage where  $D$  is independent of  $E$ .

Disregarding reversal for the present, we may note that with retarded development, although the curve is similar in



shape, it is shifted on the  $\log E$  axis. The deviations with retarded development suggest that  $D$ , the density on development, does not correctly represent the mass of the photo-product, but only that minimum necessary to render the grain developable for a particular development energy (compare Chap. V., p. 188) on the free energy in development. The *grain* has been shown (p. 83) to be the unit in development, hence while the photo-product continues to increase per grain, for normal development (maximum available energy of developer) this increase is of no value above a certain limit, but with retarded development it comes into play, and we may still have an ascending scale of densities in what would be for *normal* development the neutral condition. This explains the shifting of the curves for retarded development; the curves given typify the phenomena.

FIG. 38.



It is evident that the characteristic curve, highly important though it be, is not a complete epitome of the progress of the photo-chemical reaction, and as the complications of this are made evident, it will be seen that this could not be expected.

**Reversal and Solarisation.**—Few phenomena in the photographic process have excited more interest and speculation than this. That a reaction, while the exciting conditions continue, should gradually retrace or reverse its course, instead of reaching a condition of equilibrium or no further change, must necessarily extort admiration. Various forms of reversal in the photographic process are known, not all of equal interest or importance, so that a brief classification is desirable.<sup>1</sup>

(a) Continuous exposure : light or Röntgen-rays.

(b) Development slightly, then in light.

(c) Normal plate partially developed, then exposed to lamplight before fixation.

(d) Clayden effect : a very short ( $1/1000$  sec. or less) exposure to intense light, followed by diffuse light.

(e) Addition to developer of thiosulphate, and more especially thiosinamine (Waterhouse).

(f) Prolonged development of under-exposures (Guehard).

Forms (b) and (c) are of no special importance, being merely due to the printing through of the image formed by the first exposure and development. Of the others, form (e) has already been noticed in Chap. IV. Form (f), of which the following figures give an illustration,

TABLE 106.

Log E.	D <sub>1</sub> .	D <sub>2</sub> .	D <sub>3</sub> .	D <sub>4</sub> .	D <sub>1</sub> for 12 minutes.
1·00	0·072	0·080	0·050	0·020	D <sub>2</sub> „ 17 „
1·36	0·090	0·179	0·239	0·108	D <sub>3</sub> „ 25 „
1·575	0·138	0·303	0·388	0·232	D <sub>4</sub> „ 45 „

<sup>1</sup> Cf. also R. W. Wood, *Phil. Mag.*, 1903, 577.

has been dealt with at some length by A. Guebhard,<sup>1</sup> who does not attempt a specific explanation. Form (*e*) appears to be largely an accelerated case of form (*f*), this being due to the formation of a solution of colloidal silver in the unexposed bromide, which, in the absence of development germs, is coagulated and precipitated according to quite other laws than those of development. Obviously only forms (*a*) and (*d*) are relevant to the true photo-chemical reaction. Of these the Clayden effect has been investigated by R. W. Wood (*loc. cit.*), and may probably be considered as an exaggerated case of the departures from the Bunsen-Roscoe law noted in the next section.

The ordinary type of reversal (*a*) is very difficult to account for satisfactorily, more especially as the immense exposures required have resulted in but little quantitative work. Various theories have been proposed. Abney considers that two actions are at work, one producing the normal latent image, the other (solarising influence) a less reducible product, this action ultimately predominating. He associates reversal and the solarising action with the influence of oxygen. Englisch<sup>2</sup> also supports the theory of two actions.

Hurter and Driffeld (*loc. cit.*) and Sterry (*Phot. Journ.*, 1898), who held the physical view of the latent image, but allowed that free bromine destroyed it, supposed that reversal was due to an ultimate dissociation of the halide, the free bromine formed destroying the latent image. Sterry (but see later) subsequently modified this to suit his theory of primary and secondary development,<sup>3</sup> his view now being that neither halogens nor oxidising agents destroyed the latent image, but only retarded "secondary" development.

Precht<sup>4</sup> considered that reversal was largely a development phenomenon. This is supported by the fact that with retarded development (p. 211) the reversal point is pushed much farther back.

That the released bromine, at a certain stage of exposure, gives rise to reversal by an action *subsequent to exposure*,

<sup>1</sup> *Bull. Soc. Franc. Phot.*, 1903, **19**. 64; *Journ. de Phys.*, 1905, 334.

<sup>2</sup> *Schwarzungsgesetz d. Phot. Platt.*, Halle, Knapp.

<sup>3</sup> *Phot. Journ.*, 1904, **44**. 50.

<sup>4</sup> *Physik. Zeitschr.*, 1902, 426.

appears probable from the fact that bathing the film with nitrite or sulphite solution retards reversal. This is cited by Abney as demonstrating the action of oxygen in reversal, but it is equally applicable to that of free halogen. Precht showed further<sup>1</sup> that soaking the plate in a developer solution (edinol sulphite) before exposure, with subsequent development in 10 per cent. soda, greatly extended the neutral period and retarded reversal. In the region of normal exposure and the neutral zone no greater differences are to be observed than between plates exposed wet and dry. (For this, see later.) But while with the normal plate about 9000 H.M.S. bounds the neutral zone, and reversal then commences, with developer present the limit is extended to some 400,000 H.M.S., or about 44 times the former value. Plates containing reducing substances present may give the maximum density from, say, 650 H.M.S. to 400,000 H.M.S.

A reversing action of the released bromine may also be deduced from the failures of the Bunsen and Roscoe "reciprocity law."

**Failure of a Photo-chemical Law.**—If the exposure of a plate be  $E$ , then—

$$E = It$$

where  $I$  is the intensity of the incident light, and  $t$  is the time of exposure. According to Bunsen and Roscoe, this law holds for a photo-chemical reaction independently of the values of  $I$  or  $t$ .

It was first pointed out by Sir W. de W. Abney in 1893 that this law did not hold absolutely for photographic plates,<sup>2</sup> though Miethe<sup>3</sup> had suggested a photo-chemical induction period. This was confirmed by Eder<sup>4</sup> and Schwarzschild,<sup>5</sup> who proposed the formula—

$$E = It^P$$

where  $P$  is slightly less than unity.

<sup>1</sup> *Zeit. wiss. Phot.*, 1905, **III**. 79.

<sup>2</sup> "Chemical Action and Exposure," *Phot. Journ.*, Oct., 1893; also "The Failure in a Phot. Law with Very Intense Light," *J. C. C.*, **8**. 46.

<sup>3</sup> Miethe, *Inaug. Diss. Göttingen*, 1889.

<sup>4</sup> *Handbuch*, 2nd vol., and *Jahrbuch*, 1899, p. 457.

<sup>5</sup> *Phot. Corr.*, 1899, p. 171; and *Beiträge zur Phot. Photem. d. Gestirne*.

This does not agree with the investigations of Abney nor with the work of Englisch,<sup>1</sup> both of whom find P variable.

A typical example of Abney's results is as follows :—

TABLE 107.

Intensity of light.	Exposure, <i>t</i> .	<i>I</i> <i>t</i> .	Effective exposure.
$\frac{1}{144}$	1440	10	0.40
$\frac{1}{64}$	640	10	0.51
$\frac{1}{36}$	360	10	0.55
$\frac{1}{16}$	160	10	0.65
$\frac{1}{4}$	40	10	0.79
1	10	10	1.0

And the following is an example of Englisch's :—

TABLE 108.

Intensity.	Time to get same results.	<i>I</i> <i>t</i> .	Effective exposure.
$\frac{1}{25}$	152.5	6.5	0.77
$\frac{1}{16}$	97.6	6.1	0.82
$\frac{1}{9}$	52.2	5.8	0.86
$\frac{1}{4}$	21.6	5.4	0.93
1	5.0	5.0	1.00

Inasmuch as the subject appeared to be one of some considerable importance from its bearing on the theory of the latent image, we decided to attempt to repeat these results.

In Abney's and Englisch's experiments the intensity of the light was varied by varying the distance of the light-source, and in one experiment of Abney's by the use of a Spurge sensitometer. The variation of intensity by variation of distance requires, for accurate work, somewhat complicated apparatus of considerable size, and also greatly limits the range of variation possible. We therefore decided to attempt to use other means.

First attempts included a variable diaphragm moving in front of ground-glass surfaces. This was abandoned in consequence of the fact that the diaphragm mount always cut off part of the light, and gave unequal exposures to different parts of the plate. We next obtained a metal frame and a series

<sup>1</sup> E. Englisch, *Das Schwärzungs-gesetz*, published by W. Knapp, Halle.

of neutral-glass tints, which could be placed either singly or together in the path of the light-beam. These failed to give consistent readings, in consequence of the selective absorption which they exhibited, especially in the ultraviolet region. Unfortunately no neutral tint glass can be obtained which is black, all is either green or violet. The adoption of photographic densities made on Barnet gaslight plates, which give no selective absorption when developed with ferrous oxalate, solved this difficulty. With these chlorobromide plates the scatter is very small, and in order to neutralise any effect the opening was always covered with a piece of ground glass.

Three burners were used, large and small openings to one standard small burner, and also a large water-cooled burner. These burners were calibrated in terms of the primary pentane standard as follows: The small opening of the small burner (which is presumably the most accurate) was first calibrated. The pentane standard taken was the arithmetic mean between a 1-candle Simmance standard and a 10-candle Vernon Harcourt standard belonging to Messrs. Kodak, Limited. The pentane used was procured from the makers of the standards.

The calibration was performed thus: A number of plate-glass slips,  $1\frac{1}{2}$  inch wide, were obtained, coated by Mr. Wratten with an ordinary emulsion. Upon one side of these a series of graduated exposures were impressed by the pentane burners. The other side was then exposed behind the sector-wheel to the acetylene standard, and the slips were developed and measured.

From the true inertia as given by the pentane, and the apparent inertia given by the acetylene, the actinic intensity of the acetylene flame at the dark slide could be calculated in terms of pentane candlemetres.

The results obtained, for instance, were for  $\log i$ —

1 candle pentane—	Acetylene—
0'430 } mean 0'465	1'905
0'500 }	1'910
10 candle pentane—	1'930
0'450 } mean 0'454	1'890
0'451 }	
0'460 }	
Total mean . . 0'458	Mean . . 1'909

This gives the difference between the log  $i$ 's true and apparent as 0.549.

Whence the actinic intensity of the acetylene is 3.54 candle-metres.

This standard can then be multiplied very simply by impressing  $1\frac{1}{2}$ -inch strips on one side with a known series of exposures by the acetylene burner, and then exposing the other to the burner to be calibrated.

In this way the three burners mentioned, with the ground-glass and clear glass in position, were calibrated, and the intensities were found to be—

- (1) Small opening of small burner . . 2.24 candlemetres.
- (2) Large opening of small burner . . 6.00 candlemetres.
- (3) Large water-cooled burner . . . 84.5 „ „

The densities prepared were carefully measured in the photometer, the clear glass being taken as zero, and were found to be—

TABLE 109.

Plate.	Density.	Opacity.
0	0	1
1	0.542	3.48
2	1.120	13.29
3	2.48	302.5
4	4.80	63100

It is clear that with these burners and densities we have an accurately known intensity range from 84.5 candlemetres (or, with no ground-glass screen, 198.5 candlemetres) downwards.

The exposures given varied from 0.1 second to 2 hours, so that this method gave an enormous range of intensities.

The method employed for giving short exposures which could not be timed accurately merits a brief description, inasmuch as it has always been somewhat of a stumbling-block in investigations of this kind. Shutters of various kinds are difficult to make trustworthy. Abney used a drop shutter with jaws of varying length, which appears to have been quite satisfactory. The method which we adopted was to run the

sector-wheel very slowly by greatly gearing down the engine; it is possible to retain an even drive from a hot-air engine at only 30 revolutions per minute, and then to expose the plate for one revolution only by means of the flap shutter. In this way the sector itself acts, so to speak, as a graduated focal plane shutter, giving continuous exposures from  $\frac{1}{2}$  second (top sector at 30 revolutions) to  $\frac{1}{2048}$  second (bottom angle at 60 revolutions).

Moreover, since each plate exposed contains several different sectors, it is possible to find the development factor of the plate, which is of great assistance.

The specific result it was desired to attain in this work was to find the value of  $I t$  necessary to give the same effect with different values of  $I$ , and then to plot a curve of  $I t$  against  $I$ . If there were no effective failure of the reciprocity law, this value of  $I t$  would be a constant, and the curve would be a straight line parallel to the  $I$  axis. Otherwise it would be a curve, and from its shape some conclusions as to the amount and type of the failure might be drawn. It was of particular importance to decide —

- (1) whether the failure was proportional to  $t$ ;
- (2) whether the failure was dependent on the absolute value of  $I t$ ;
- (3) whether the failure noticeably varied in extent with different plates.

A Wratten ordinary (batch 6693) plate was first measured, and the exposure necessary to give an exposure of 16 times the inertia, *i.e.* to obtain a density of 1 with 5 minutes' development with  $\frac{N}{10}$  ferrous oxalate at 20° C., was found for many different intensities.

This was done by trial and error; thus—

$$\begin{array}{l} \text{Big opening of small burner} = 6.0 \\ \text{Big opening of small burner} \left. \begin{array}{l} \text{with densities 1 and 2} \end{array} \right\} = \frac{6.0}{3.48 \times 13.29} \end{array}$$

which is the intensity in candlemetres.

With this exposure we try  $I t = 13.3$ ,  $t = 103$  seconds. Resulting density, 0.872.



Recalculating from known value of  $\gamma$ , try  $I t = 15.5$ ,  $t = 120$ ; then  $D = 0.998$ .

(1) In this way the following results were obtained:—

TABLE IIO.

I.	$t$ (to give $D = 1$ ) secs.	$I t$ .	Log ( $1 \times 1000$ ).
84.5	0.204	17.2	4.927
6.0	2.59	15.5	3.720
1.71	9.61	16.4	3.232
0.452	34.4	15.5	2.655
0.130	120	15.5	2.114
0.0198	931	18.4	1.296
0.0074	4760	35.1	0.869
0.0056	6460	36.2	0.750

This result shows that the failure is not a simple function of  $t$ , and the result agrees excellently with Englisch's results.

(2) The dependence of the failure on the total value of  $I t$  was measured in the following way:—

Two series of continuous exposures were given. One by one revolution of the sector wheel with a duration of 4.14 seconds, and an intensity of 84.5, giving exposures of 179, 89.5, 45, . . . etc., C.M.S., and the other with an intensity of 0.130, giving  $I t = 89.5$ , 45, . . . etc., when  $I t$  unity for 84.5 is taken as 17.2, and  $I t$  unity for 0.130 as 15.5.

*Results—*

TABLE III.

Log $I t$ .	$D_{(I = 84.5)}$ .	$D_{(I = 0.130)}$ .
2.25	1.724	—
1.95	1.520	—
1.65	1.330	1.309
1.35	1.020	1.020
1.05	0.707	0.704
0.75	0.432	0.438
0.45	0.232	0.219
0.15	0.065	0.072

These results show clearly that the total value of  $I t$  does not influence the extent of the failure.

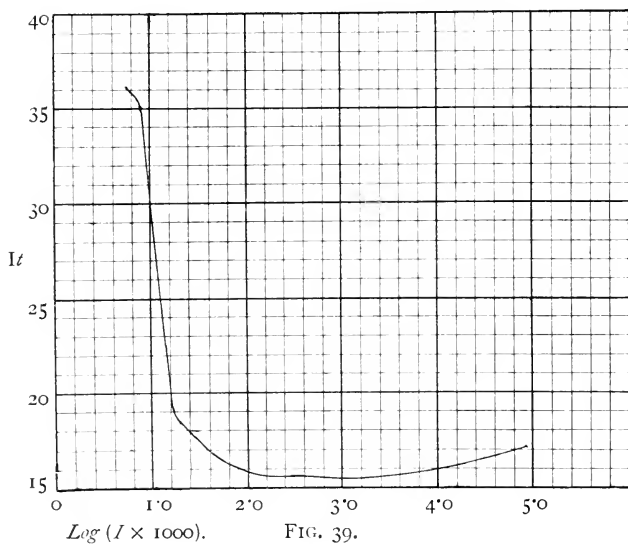


FIG. 39.

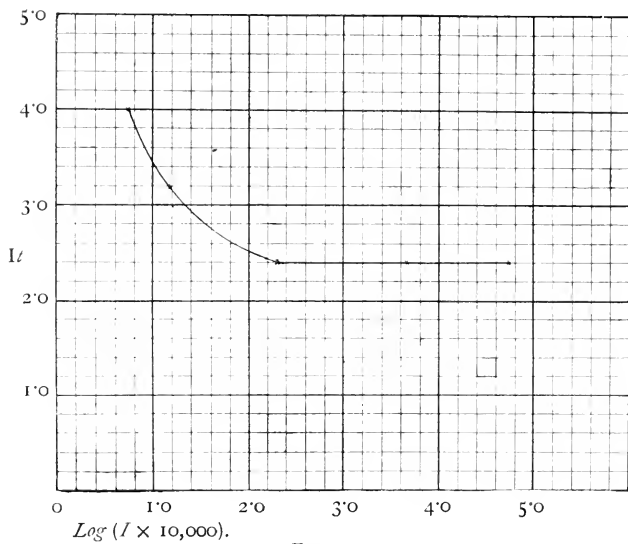


FIG. 40.

(3) The whole of the measurements were repeated on the Wratten "Speed" plate.

*Results—*

TABLE 112.

I.	$t_{\text{(for } D = 1\text{)}}$ .	$It$ .	Log ( $I \times 10,000$ ).
6.0	0.40	2.4	4.72
0.452	5.32	2.4	3.654
0.0198	121	2.4	2.296
0.00149	2160	3.2	1.173
0.000545	7370	4.0	0.736

This result shows that the Wratten ordinary and speed curves are almost identical in shape and type.

Now, for the straight portion of the  $It$ ,  $I$  curve, if we measure the inertias of the Wratten ordinary and speed plates, we get—

$$\log i \text{ speed} = 1.33$$

$$\log i \text{ ordinary} = 0.45$$

whence—

$$\frac{i \text{ ordinary}}{i \text{ speed}} = 13.2$$

And if we take the departures from the straight line from the  $It$ ,  $I$  curve—

$$\text{Departure point for ordinary plate} = I = 0.01$$

$$\text{Departure point for speed plate} = I = 0.001$$

So that the reciprocity failure may be considered to start at much the same point *relatively to the inertia points* in the two plates.

The result is opposed to Abney's conclusions, and possibly requires confirmation, which it is very difficult to obtain. An attempted measurement of the failure for gaslight plates was stopped by the enormous exposures required.

An effect which is evidently closely related to the failure of the reciprocity law is the failure of a series of intermittent exposures to produce the same effect as the equivalent continuous exposure. This effect was first shown to exist by A.

and L. Lumière, in 1881; but the first important and complete investigation on the subject is that of Abney. The whole effect has, however, been discussed with great acuteness by Englisch in *Das Schwarzungsgesetz*.

Inasmuch as we always use a sector-wheel in sensitometry, it appeared desirable to determine whether the intermittency correction would be of appreciable dimensions in ordinary work. The method of work adopted was simply to run the sector-wheel at different speeds by varying gearing.

Two Wratten ordinary plates exposed together for five minutes—

(1) at 1520 revolutions per minute.

(2) at 9·5 revolutions per minute.

*Results—*

TABLE 113.

Log E.	D <sub>1</sub> .	D <sub>2</sub> .
2·60	1·906	1·816
2·30	1·630	1·520
2·00	1·368	1·337
1·70	0·988	1·040
1·40	0·632	0·725
1·10	0·307	0·470
0·80	0·105	0·245
0·50	0·023	0·0713
0·20	—	0·021

This result shows very clearly the great effect of the intermittency correction upon the bottom exposures. The conclusion from the results obtained was that for practical sensitometry, if the sector-wheel were not driven above 100 revolutions per minute, then the intermittency error would be negligible even for slow plates.

The theory adopted by Englisch (*Das Schwarzungsgesetz*), to explain the results both of diminished intensity and also of intermittent exposure, is that they are caused both by an induction loss and also by a fading loss. The fading loss is worthy of primary consideration, as it must be by far the greatest factor. This loss must go on during the whole time of exposure, and must therefore be due to a reverse reaction tending

to produce the opposite effect to exposure. Now we know that a reverse oxidation reaction to exposure exists, since we can catalyse it by means of "desensitisers." The question as to whether a "desensitised" plate will show a greater failure of the reciprocity law was therefore investigated, and it was found that a greater failure occurred.

Of the existence of the induction loss we have but little satisfactory evidence; but Englisch appears to have proved that it has some small effect, and it would give a satisfactory explanation of Abney's results with very intense light sources. When Englisch styles this loss the ordinary "photo-chemical induction," he appears to be on doubtful ground, inasmuch as the whole photographic effect should probably be placed in the period of photo-chemical induction.

Various "molecular" and "strain" hypotheses have been evolved to account for these phenomena, but they are sufficiently well explained by the peculiar nature of photo-chemical equilibria. Abegg<sup>1</sup> has correlated with these facts the difference in photographic effect obtained when plates are exposed through the glass-side and from the front, precautions being taken to allow for the absorption of light by the glass and the action of the developer. From the investigations of Luggin and Luther,<sup>2</sup> it appears that the continuous exposure of silver halides to light results in an equilibrium condition, whereby every light-intensity is balanced by a definite halogen-potential (whether expressed as gas-pressure, electric potential, or solution pressure). The natural equilibrium will not be reached on ordinary plate-exposures for two reasons; first, that the exposure is too short, and secondly, that the halogen is removed, either by diffusion or by combining with the gelatin. Now, diffusion will be easier from the film-side than from the glass-side, and to this Abegg attributes the aforementioned difference in plates exposed from the front and through the glass. Immediately the incident light is cut off, any free halogen present combines with the reduction product to the original halide. The intermittency effects are all in

<sup>1</sup> *Sitz. ber. Wien. Akad.*, 1900, 109. 1.

<sup>2</sup> *Zeit. phys. Chem.*, 23. 577, 1897; *Zeit. phys. Chem.*, 1899, 30. 628.

good agreement with this view, since the reverse reaction would have the greater effect (*a*) the longer the pause, and (*b*) the more numerous the pauses, a pause being the period of no illumination.

The failure of the reciprocity law with small intensities is less easily explained, and it is not certain that this is not involved in processes antecedent to the liberation of free halogen. We have to consider, however, that in the removal of the free halogen, both processes are proportional to the mass of this, and that with low intensities of light the equilibrium potential of halogen is lower, so that even while the light is acting, the reverse reaction is more potent than with higher intensities. The mere formulation of all these factors is valueless till we possess more information as to the processes in detail.

**The Decay and Destruction of the Latent Image.**—Whilst the latent image in the Daguerreotype process was so evanescent that development was necessary shortly after the exposure, it is well known to photographers that the image on dry plates is comparatively permanent, so that six months or a year may elapse and yet well-exposed negatives be obtained. Such data, however, are generally without control. C. H. Bothamley<sup>1</sup> found that plates exposed two and a quarter and four years before gave negatives in no wise different from those immediately developed. Gaedicke states, however,<sup>2</sup> that the latent image gradually loses "tone and intensity." Baekeland<sup>3</sup> brings forward several cases of a decay of the latent image. From his own experiments directed to this point he concludes—

*Photo-retrogression*, or slow disappearance of the latent image, takes place with all halide emulsions; more with under-exposed than over-exposed plates. It may, under certain conditions, become apparent in forty-eight hours, increasing till the image has totally vanished. It occurs more rapidly at high temperatures, and is more evident in a damp than in a dry atmosphere. An acid reaction of the film favours it, but

<sup>1</sup> *Eder's Jahrb.*, 1894, 279.

<sup>2</sup> *Eder's Jahrb.*, 1901, 392.

<sup>3</sup> *Zeit. wiss. Phot.*, 1905, III. 58.

it is less appreciable if the emulsion be neutral or slightly alkaline.

In considering all evidence as to spontaneous decay of the latent image, the tendency of photographers to confuse the developing properties of a plate with its sensitiveness to light must be borne in mind. In a former chapter<sup>1</sup> we showed that plates, on keeping, especially if stored in an unfavourable atmosphere, greatly changed in their rate of development, the value of  $K$ , the velocity coefficient, sinking to as much as one-third of its former value in six months. It is obvious that without quantitative measurements the diminished density obtained might readily be ascribed to a decay of the latent image. However, there seems little doubt that such a change does take place, and while the process of exposure appears to result broadly in a reduction, the retrogression of the image appears to be an oxidation phenomenon. That free halogen will destroy the latent image has long been maintained.<sup>2</sup> Also that oxidising agents destroyed it. Thus Eder and Abney used chromic acid, Schaum and Braun persulphate, Abegg<sup>3</sup> nitric acid, while the action of other oxidising solutions has also been shown to be inimical, as ammoniacal  $\text{CuCl}_2$ ,<sup>4</sup>  $\text{CuSO}_4$ , and  $\text{HgCl}_2$ .<sup>5</sup> The investigation of the action of halogens on the photo-product has been carried out quantitatively by Luther (*loc. cit.*) and Baur,<sup>6</sup> whose work forms an important bulwark for the subhalide theory. Luther found a jump in the potential of an  $\text{Ag}:\text{Ag X}$  electrode in  $n/10$   $\text{HX}$ , treated with increasing quantities of halogen, at a percentage corresponding to  $\text{Ag}_2\text{X}$ . Baur, however, found that the potentials were not well defined, and concluded that the half-halide formed solid solutions in all proportions with normal halide.

<sup>1</sup> Cf. also *Proc. Roy. Soc.*, 1905, 74. 450.

<sup>2</sup> Eder, *Phot. Corr.*, 1899, 332; Englisch, *Arch. wiss. Phot.*, 1899, I. 282; Meldola, *Chem. of Phot.*, 1891, pp. 198-232; Lüppo-Kramer, *Phot. Corr.*, 1901, 151.

<sup>3</sup> Eder, *Hdbuch.*, III. 76; Abney, *Treat. on Phot.*; Schaum and Braun, *Phot. Mit.*, 1902, 224; Abegg, *Arch. wiss. Phot.*, 1899, I. 15.

<sup>4</sup> Lumière, *Bull. Soc. Fran. Phot.*, 1887.

<sup>5</sup> Reiss, *Phot. Centr.*, 1902, 16.

<sup>6</sup> *Zeit. phys. Chem.*, 45. 618.

It is certain that most who have worked with the "photo-halides," whether prepared synthetically or by light action, will agree that they behave, as Carey Lea says, "like homogeneous mixtures of the nature of lakes," or, in modern terminology, solid solutions. Further, the equilibrium potential of an oxidising or halogenising agent appears to depend upon the composition of the photo-halide, a greater potential being required to destroy the half-halide when its concentration is slight. We shall refer again to this point in dealing with the action of oxidising agents.

**Action of Oxidising Agents on the Latent Image.**—While the action of free halogens, or of halogen ions plus oxidiser, is explicable as due to rehalogenisation, the action of plain oxidising agents is also of interest. It has been maintained by some that these do not destroy the latent image, but merely retard development. Mr. Sterry<sup>1</sup> found that when a sensitive film is soaked between exposure and development with a solution antagonistic to the developer, the gradation of the negative obtained is entirely altered, this alteration depending upon the strength of the solution and its time of action. Under certain conditions an entirely new scale may be obtained, giving correct gradation from the first impression to a point beyond reversal, as shown in ordinary development. Potassium bichromate solution or permanganate was used, the film being merely rinsed before treatment by the developer. Mr. Sterry considered that development consisted of two operations, first, the reduction of the affected halide, then the intensification of this by silver from the surrounding halide; this he termed secondary development, and held that the bichromate or other oxidiser in some way retarded the secondary development.

We have made an investigation of this question, with the following results :—

**Method of Work.**—Owing to the fact that at the time this research was undertaken the exposure machine had been redesigned and a new one was being made, we were unable to

<sup>1</sup> *Phot. Journ.*, 1904, 54. 50.



employ it for this work. Exposures were therefore made behind a negative consisting of a series of carefully measured densities, and these exposures were made to one of three burners of standard power. Only one of these could be really trusted, however, and this one alone was therefore used wherever variations in the total amount of exposure could affect the results.

These three acetylene burners were measured against the pentane standard, and were found to give at the standard distance.

No. 1 . . . 2 candlemetres (correct).

No. 2 . . . 20 candlemetres (approximate).

No. 3 . . . 730 candlemetres (approximate).

Usually exposures of 400 C.M.S. were used in this work. The exposure actually used in any experiment can be seen from the log E table given.

The densities of the test negative were as follows :—

TABLE 114.

Degree.	Density.	Opacity.	Transparency.	Log T $\times$ 400.
1	0	0	1	2.60
2	0.341	2.19	0.456	2.261
3	0.500	3.16	0.317	2.102
4	0.680	4.78	0.209	1.923
5	1.011	10.25	0.0975	1.591
6	1.390	24.55	0.0408	1.213
7	1.739	54.8	0.01822	0.863
8	2.086	121.9	0.00821	0.516
9	2.460	288.1	0.00346	0.140

All plates were soaked, developed, etc., in the developing thermostat at 20° C.

The developers used were—

(1) The decinormal ferrous oxalate developer described before.<sup>1</sup>

<sup>1</sup> See also *Phot. Journ.*, February, 1903.

(2) A  $\frac{N}{20}$  hydrokinone developer, containing—

$\frac{N}{20}$  hydrokinone,  
 $\frac{N}{20}$  soda sulphite,  
 $\frac{N}{5}$  sodium carbonate.

The chromic acid solutions were prepared from a standard dinormal solution which had been checked against ferrous sulphate solution standardised against  $\frac{N}{10}$  permanganate, which had been prepared with  $\frac{N}{10}$  oxalic acid, this being brought to the usual sulphuric acid standard. The permanganate was also checked against  $(\text{FeAm}_2(\text{SO}_4)_2)$ .

**On the Addition of Chromic Acid to the Developer.**—If chromic acid be added to the developer itself, its only effect is to immediately oxidise some of the developing agent; as, however, we were informed that this method was being tried, we decided to conduct a few experiments to confirm this.

Wratten ordinary plates were taken and exposed.

- |     |                        |              |   |                    |
|-----|------------------------|--------------|---|--------------------|
| (1) | Two plates, 1A and 1B, | developed in | $\frac{N}{10}\text{Fe}\bar{\text{O}}$                                   | for 5 and 10 mins. |
| (2) | „ 2A „ 2B „            | „            | $\frac{N}{10}\text{Fe}\bar{\text{O}}$ with $\frac{N}{1000}\text{CrO}_3$ | „                  |
| (3) | „ 3A „ 3B „            | „            | „ $\frac{N}{100}\text{CrO}_3$   | „                  |
| (4) | „ 4A „ 4B „            | „            | „ $\frac{N}{50}\text{CrO}_3$  | „                  |

## Results—(1) 1A and 1B—

TABLE 115.

Log E.	D <sub>A</sub> .	D <sub>B</sub> .
2.102	1.796	2.45
1.923	1.692	2.34
1.591	1.387	1.98
1.213	1.10	1.58
0.863	0.806	1.152
0.516	0.512	0.742
0.140	0.287	0.414

Plotting the curve, the slopes  $\gamma_1$  and  $\gamma_2$  are  $\gamma_1 = 0.87$ ,  $\gamma_2 = 1.19$ , whence  $\gamma_\infty = 1.38$ ,  $\kappa = 0.200$ ; also  $\log i = 1.98$ .

*Note.*—Curves are not given simply to show  $\gamma$ 's, as it does not appear necessary.

## (2) 2A and 2B—

TABLE 116.

Log E.	D <sub>A</sub> .	D <sub>B</sub> .
2.602	1.724	2.83
2.26	1.58	2.45
2.10	1.53	2.23
1.92	1.44	2.12
1.59	1.27	1.80
1.213	1.025	1.41
0.863	0.751	1.01
0.516	0.472	0.568
0.140	0.260	0.330

$\gamma_1 = 0.75$ ,  $\gamma_2 = 1.05$ , whence  $\kappa = 0.184$ ,  $\gamma_\infty = 1.27$ ,  $\log i = 1.93$ .

## (3) 3A and 3B—

TABLE 117.

Log E.	D <sub>A</sub> .	D <sub>B</sub> .
2.60	1.55	2.76
2.26	1.37	2.38
2.10	1.31	2.23
1.92	1.20	2.05
1.59	1.03	1.70
1.213	0.846	1.28
0.863	0.620	0.916
0.516	0.382	0.584
0.140	0.201	0.286

$\gamma_1 = 0.63$ ,  $\gamma_2 = 1.00$ , whence  $\kappa = 0.108$ ,  $\gamma_\infty = 1.52$ ,  $\log i = 1.96$ .

(4) 4A and 4B—

TABLE 118.

Log E.	D <sub>A</sub> .	D <sub>B</sub> .
2·60	1·26	2·19
2·26	1·193	2·00
2·10	1·124	1·906
1·92	1·074	1·77
1·59	0·920	1·50
1·213	0·682	1·163
0·863	0·500	0·850
0·516	0·313	0·500
0·140	0·112	0·207

$\gamma_1 = 0·55$ ,  $\gamma_2 = 0·88$ , whence  $\kappa = 0·094$ ,  $\gamma_\infty = 1·50$ ,  $\log i = \bar{1}·94$ .

The curve of  $\gamma$  against time of development was also plotted for a developer containing  $\frac{50}{N}\text{CrO}_3$ .

*Results—*

$t$ (minutes)	2	4	5	8	10	16	$\infty$
$\gamma$	0·10	0·38	0·55	0·82	0·88	1·25	1·45
taking $\gamma_\infty = 1·50, \kappa = \frac{1}{t} \log_{10} \frac{\gamma_\infty}{\gamma_\infty - \gamma_t} =$	·031	0·0401	0·043	0·383	0·049	—	—
Mean $\kappa_{(t)}$ for this experiment = 0·098.							

Tabulating these results, we get—

TABLE 119.

CrO <sub>3</sub> .	K.	$\gamma_\infty$ .	Log $i$ .
0	0·200	1·38	$\bar{1}·98$
$\frac{N}{1000}$	0·184	1·27	$\bar{1}·93$
$\frac{N}{100}$	0·108	1·52	$\bar{1}·96$
$\frac{N}{50}$	0·094	1·50	$\bar{1}·94$

We may hence conclude that  $\log i$  and  $\gamma_\infty$  are independent of the  $\text{CrO}_3$ , while  $\kappa$  diminishes owing to the oxidation of the developer.

Now, in 100 c.c. of developer we have 10 c.c.  $\frac{N}{I}\text{FeSO}_4$ .

$\frac{N}{1000}$	$\text{CrO}_3$ neutralizes 0.15 c.c.		
$\frac{N}{100}$	"	"	1.5 "
$\frac{N}{50}$	"	"	3 "

Therefore we should get, taking  $\gamma_\infty$  at 1.50 and calculating  $\kappa$  from it—

TABLE 120.

$\text{CrO}_3$ .	$\kappa$ found.	$\kappa$ calc. from oxidation.
0	0.165	(0.165)
$\frac{N}{1000}$	0.130	0.161
$\frac{N}{100}$	0.106	0.139
$\frac{N}{50}$	0.094	0.115

These numbers seem to show fairly (the errors in this work are unfortunately great in calculations of  $\kappa$ ) that the effect is simply due to oxidation.

**On the Effect of Dipping Plates in  $\text{CrO}_3$  before Development.** Part 1.—*Developing immediately after dipping, effect on  $\kappa$ .*

The plate was rotated in chromic acid for the given time before developing. At first we tried blotting, and then washing with a stream of water in order to get the acid off the surface, but eventually we decided to rotate for a fixed time in water after chromating, as these other methods left irregular surface markings.

(1)  $\gamma, t$ , curve for  $\frac{N}{10,000} \text{CrO}_3$

Plates dipped 1 minute in  $\frac{N}{10,000} \text{CrO}_3$ , then washed 1 minute in water, then developed 2, 4, 8, 16, 64 minutes.

TABLE 121.

Log E.	D <sub>2</sub> .	D <sub>4</sub> .	D <sub>8</sub> .	D <sub>16</sub> .	D <sub>32</sub> .
2·60	0·647	1·59	2·47	3·96	—
2·26	0·584	1·446	2·25	2·96	—
2·10	0·604	1·357	2·19	2·83	—
1·92	0·554	1·276	1·91	2·56	3·44
1·59	0·494	(crack in neg.)	1·624	2·16	2·56
1·213	0·400	0·876	1·29	1·67	1·91
0·863	0·313	0·658	0·94	1·16	1·40
0·516	0·206	0·416	0·57	0·78	0·96
0·140	0·106	0·193	0·276	0·42	0·565

From the curves—

$$\kappa = \frac{\log_e \frac{\gamma_\infty}{\gamma_\infty - \gamma_t}}{t}$$

$\gamma_2$	$\gamma_4$	$\gamma_8$	$\gamma_{16}$	$\gamma_{64} = \gamma_\infty$
0·26	0·575	0·92	1·26	1·50
0·099	0·121	0·119	0·114	—

Mean  $\kappa = 0·118$

(2)  $\gamma, t$ , curve for  $\frac{N}{100} \text{CrO}_3$

TABLE 122.

Log E.	D <sub>4</sub> .	D <sub>8</sub> .	D <sub>16</sub> .	D <sub>32</sub> .
2·60	0·562	0·948	1·768	—
2·26	0·562	0·948	1·768	—
2·10	0·562	0·948	1·768	2·96
1·92	0·562	0·876	1·724	2·59
1·59	0·512	0·786	1·53	2·10
1·213	0·424	0·600	1·245	1·51
0·863	0·304	0·402	0·860	1·094
0·516	0·202	0·258	0·528	0·748
0·140	0·097	0·128	0·239	0·475

The curious flattening at the top accords with facts discussed later, and will be left for the present.

From the curves—

$\gamma_4$	$\gamma_8$	$\gamma_{16}$	$\gamma_{32}$	$\gamma_\infty$
0·34	0·49	0·9	1·37	1·50
0·066	0·050	0·057	0·044	—

Mean 0·058

Therefore we get for plates rotated 1 minute in the chromic acid, and then one minute in water—

TABLE 123.

Chromic.	$\kappa$ .
0	0'145 <sup>1</sup>
$\frac{N}{10,000}$	0'118
$\frac{N}{100}$	0'058

Also  $\gamma_{\infty}$  is constant.

Now, since  $\gamma_{\infty}$  is constant, and we know that the time of appearance of an image =  $a\kappa\gamma_{\infty}$ , we can calculate  $\kappa$  from the relative times of appearance with different strengths of  $\text{CrO}_3$ .

TABLE 124.

$\text{CrO}_3$ .	% strengths.	Time of appearance.	$\kappa$ (found above).	$\kappa T_a$ .	$\kappa$ (calc.) from $\kappa T_a$ .
0	0	15 secs.	0'145	2'2	0'126
$\frac{N}{10,000}$	0'001	17 "	0'118	2'0	0'112
$\frac{N}{1,000}$	0'01	19 "	—	—	0'100
$\frac{N}{100}$	0'1	25 "	0'058	1'45	0'076
$\frac{N}{50}$	0'2	40 "	—	Mean $\kappa T_a$ 1'9	0'047
$\frac{N}{20}$	0'5	70 "	—		0'027
$\frac{N}{10}$	1	$\infty$	—	—	0'000

<sup>1</sup> From other measurements for this plate.

*Second Experiment—*

TABLE 125.

CrO <sub>3</sub> .	CrO <sub>3</sub> %.	T <sub>a</sub> .	κ (where known).	κt <sub>A</sub> .	κ calc. = $\frac{2.25}{t_A}$ .
0	0	16 secs.	0.145	2.32	0.141
$\frac{N}{100}$	0.1	50 „	0.058	2.9	0.045
$\frac{4N}{100}$	0.4	200 „	Mean κT <sub>a</sub> , taking former results, also = 2.25		0.0112
$\frac{8N}{100}$	0.8	290 „			
$\frac{9.5N}{100}$	0.95	375 „	—	—	0.0078
			—	—	0.006

The main sources of minor inaccuracies in this work are due to uneven washing out.

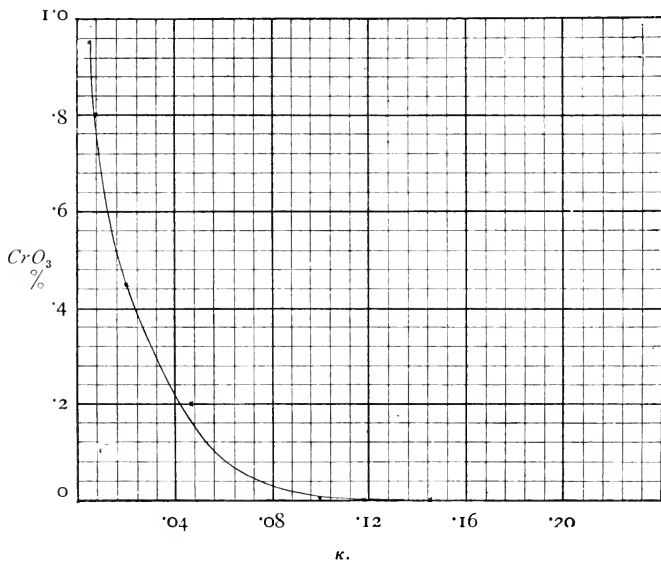


FIG. 41.



## Results—

TABLE 126.

CrO <sub>3</sub> %.	$\kappa$ .
0	0.145
0.001	0.118
0.01	0.100
0.1	0.050
0.2	0.047
0.45	0.019
0.8	0.008
0.95	0.006

See Fig. 41, which is roughly logarithmic.

We can by the "time of appearance" method study the effect of washing out the bichromate.

Plates were soaked in 0.4 per cent. chromic for 1 minute, and then rotated in water for various lengths of time.

TABLE 127.

Time washing.	$T_a$ in secs.
0	380
1 sec.	330
30 secs.	280
5 mins. {	230
10 mins. { Water changed	150
5 hrs. { at intervals. }	100

Washing out evidently merely affects the acid held in the film itself.

Also we can study the effect of immersion time on  $\kappa$ .

TABLE 128.

Plates soaked in 0.4 % CrO <sub>3</sub> .	Washed.	$T_a$ .
$\frac{1}{2}$ sec.	1 min.	35 secs.
10 secs.	"	140 "
1 min.	"	230 "
30 mins.	"	About 12 hrs.

We can, therefore, measure the velocity of the action of  $\text{CrO}_3$  on  $\kappa$ . To do this we dip the plate, and then wash the acid out as completely as possible.

(1) Velocity of action of  $\frac{\text{N}}{50} \text{CrO}_3$ —

TABLE 129.

Soaked.	$T_a$ .	$\kappa$ , taking $T_a \kappa = 15$ .
5 secs.	15	1
10 „	23	0'63
40 „	34	0'44
80 „	44	0'34
320 „	130	0'115
640 „	130	0'115

(2) Repeated for  $\frac{\text{N}}{25} \text{CrO}_3$ —

TABLE 129.

Soaked.	$T_a$ .	$\kappa$ , taking $T_a \kappa = 28$ .
5	28	1
10	35	0'8
40	76	0'37
80	110	0'25
320	210	0'134
640	240	0'117

(3)  $\frac{\text{N}}{20} \text{CrO}_3$ —

TABLE 129.

Soaked.	$T_a$ .	$\kappa$ , taking $T_a \kappa = 27$ .
5	27	1
10	35	0'77
40	50	0'54
80	80	0'34
320	—	—
640	390	0'07

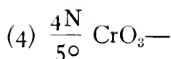


TABLE 130.

Soaking.	$T_a$	$\kappa$ , taking $\kappa T_A = 80$ .
5	80	1
10	120	0.67
40	170	0.47
80	205	0.39
320	510	0.158
640	630	0.127

Taking, from experiment with an unsoaked plate,  $T_a = 9.5$ , when  $\kappa = 0.145$ ,  $\kappa T_a = 1.38$ , we get—

TABLE 131.

CrO <sub>3</sub> per cent. 0	Time soaking. $\kappa$	0 0.145					
		5	10	40	80	320	640
0.2	$\kappa$	0.094	0.060	0.041	0.031	0.0106	0.0106
0.4	$\kappa$	0.049	0.039	0.018	0.013	0.0065	0.0058
0.5	$\kappa$	0.051	0.039	0.027	0.017	—	0.0036
0.8	$\kappa$	0.017	0.0115	0.0081	0.0067	0.0027	0.0022
0.9	$\kappa$	—	—	—	0.0043	0.0012	0.0010

Taking the last column just given, namely the  $\kappa$  when the soaking has been pushed to the limit, we get—

TABLE 132.

CrO <sub>3</sub> per cent.	$\kappa$
0	0.145
0.2	0.0106
0.4	0.0058
0.5	0.0036
0.8	0.0022
0.9	0.001

We see that the fall of velocity is proportional to the logarithm of the concentration of the chromic acid if  $\log 0.01$  per cent. be taken as 1.

If we take the table previously given, we get—

TABLE 133.

CrO <sub>3</sub> per cent.	$\kappa$ .	$0.145 - \kappa$ .	Taking $0.045 = 1$ .	Log CrO <sub>3</sub> per 100,000.
0	0.145	0	—	$\infty$
0.001	0.118	0.027	1.6	0
0.01	0.100	0.045	1.00	1
0.1	0.050	0.095	2.11	2
0.2	0.047	0.098	2.17	2.3
0.45	0.019	0.126	2.80	2.65
0.8	0.008	0.137	3.05	2.9
0.95	0.006	0.139	3.1	2.95

So that the effect varies roughly as the logarithm of the concentration.

Now, if we take the  $\kappa$  of the plate soaked 5 seconds as 1, we can compare the velocity of the fall of  $\kappa$  with different concentrations of  $\kappa$ .

TABLE 134.

Time soaked.	$\kappa \frac{N}{50}$	$\kappa \frac{N}{25}$	$\kappa \frac{N}{20}$	$\kappa \frac{4N}{100}$	Mean $\kappa$ .
5"	1	1	1	1	1
10"	0.63	0.8	0.77	0.67	0.72
40"	0.44	0.37	0.54	0.47	0.45
80"	0.34	0.25	0.34	0.39	0.33
320"	0.115	0.134	—	0.158	0.135
640"	0.115	0.117	0.07	0.127	0.108

This table fits no simple expression, but shows quite clearly that the function of action on  $\kappa$  is independent of the concentration of the CrO<sub>3</sub> employed.

The theory which appeared to me best to explain these facts was that the bichromate was adsorbed in the film, probably both to the gelatin and the silver bromide. Freshly precipitated silver bromide treated with bichromate or chromic acid takes a yellow colouration, which is not removed by long washing. Probably something of the nature of a solid solution is formed, but, in any case, the retained bichromate lowers the velocity of development by oxidising the reducer. Possibly also, the complex chromium salts formed, which would be

principally basic salts of the type investigated by Recoura, tanned the film, and so resisted development. This appeared improbable from the results with formalin, and also from the following fact. We used as a criterion to distinguish the action of the adsorbed chromic acid from tanning or destruction of the latent image, the use of a subsequent bath of a reducing agent not sufficiently powerful to develop, but which would reduce the chromic acid. Sulphite of soda was found efficient, and the following measurements show that if sulphite of soda be applied *immediately* after immersion in the chromic acid, then the velocity, and also the mass of the latent image, are unaffected.

TABLE 135.

A, in  $n/100$   $\text{CrO}_3$  ; B, ditto, and 10 minutes in  $n/10$   $\text{Na}_2\text{SO}_3$  ;  
C, no chromic.

No.	Log E.	$D_A$ .	$D_B$ .	$D_C$ .
2	1.36	0.014	0.080	0.140
3	1.575	0.108	0.220	0.231
4	1.80	0.218	0.401	0.427
5	2.14	0.313	0.594	0.663
6	2.42	0.417	0.838	0.852
7	2.71	0.542	0.976	1.052
8	3.01	0.601	1.180	1.215

The action of sulphite also brought the time of appearance back to its former value.

Hence it appears that the action of chromic acid applied immediately prior to development is simply to lower the velocity of development by oxidation of the developer. The sulphite, reacting with the chromic acid, would form basic chromic compounds, and it is interesting to note that their tanning action on the film did not diminish the rate of development. The "tanning" theory has already been noted under fixation, and no evidence in its favour found. Experiments on the "dialysis" of various solutions through gelatin films diversely treated were made by Mr. Haddon<sup>1</sup> in 1897, and show that tanning the film does not modify the diffusivity very much.

<sup>1</sup> *Phot. Journ.*, 1897, 22. 224.

Haddon gives the percentage quantity of various salts passing through different gelatin septa in the same time some of his data are reproduced.

TABLE 136.

Substance.	Oxidised pyroseptum.	Chrome alum.	Plain gelatin.
$\text{Na}_2\text{S}_2\text{O}_3$ . . .	53'0 per cent.	32'75 per cent.	38'25 per cent.
KBr . . . .	57'0 "	56'0 "	56'5 "
$\text{Na}_2\text{CO}_3$ . . .	40'3 "	30'6 "	37'6 "
$\text{Na}_2\text{SO}_3$ . . .	67'5 "	66'0 "	73'0 "
$\text{HgCl}_2$ . . .	50'0 "	37'5 "	40'0 "
Pyrogallol . .	28'0 "	44'0 "	37'0 "
Ferrous oxalate <sup>1</sup>	63'0 "	61'0 "	64'0 "

It will be seen that there is no very marked effect apparent with hardened gelatin, although the relative results differ somewhat with different salts.

We also made a few experiments on the formation of silver chromate. Cylinders of gelatine treated with formalin and weak bromide water, again washed, were soaked in bichromate solution, and then stood in silver nitrate solution. No appreciable difference was found in the rate of formation of the rings of precipitated  $\text{AgCrO}_4$  (cf. p. 205). Hence we conclude that the fall of K is solely due to oxidation of developer by adsorbed bichromate. It is hardly possible to judge the amount adsorbed, although  $\Delta K$  should be some measure. Generally in adsorption or solid solution the amount adsorbed follows some form of Dalton's distribution law, that is,  $\frac{c}{c^n} = \text{constant}$ ,<sup>2</sup> the coefficient  $n$  expressing the molecular complexity of the body in the new solvent. In this case  $\frac{c}{\Delta K} = \frac{c}{\log c} = \text{constant}$ , approximately, not agreeing with above law. But chromic acid is an equilibrium of the type  $\text{Cr}_2\text{O}_7'' \rightleftharpoons \text{CrO}_3 + \text{CrO}_4''$ ,<sup>3</sup> so that the relation would not be simple.

<sup>1</sup> Own experiment.

<sup>2</sup> Cf. Zacharias, *Zeit. phys. Chem.*, **39**. 374.

<sup>3</sup> Abegg and Cox, *Zeit. phys. Chem.*, 1904. **48**. 725.

**Destruction of Latent Image : Effect of Oxidising Agents on  $\gamma_x$  and Log  $i$ .**—Since the sulphite reaction allows us to destroy the chromic acid remaining in the film, it becomes possible to ascertain if, with increased time, the oxidiser does destroy the latent image. This is shown by the following experiment. Two plates, A and B, were taken, A being exposed; they were then chromated together in  $n/50$   $\text{CrO}_3$  for one minute, washed for ten minutes, and dried in the drying cupboard. When dry B was exposed, and both developed immediately; then if the action on K by adsorption is the only one taking place, we should expect the two plates to give equal densities. Actually plate B developed a full density, plate A nothing whatever. Hence it appears that the prolonged action of the chromic acid in the film had destroyed the latent image. This was further investigated by treating the plates with  $\text{CrO}_3$ , leaving for a given time, sulphiting, and then developing. Any fall in  $\gamma$  will be due to a change of  $\gamma_x$ . From early experiments we concluded that only  $\gamma_x$  was affected, while the rate of action depended largely on the concentration of the chromic acid, being proportional to the second or third power of this.

We made some experiments with one concentration of chromic acid,  $n/50$ , for different times, leaving the plate in the bath, from which we conclude that at first  $\gamma_x$  is chiefly affected, but subsequently log  $i$  is also increased. A few experiments with varied concentration indicated that the effect on log  $i$  is greater as the chromic acid concentration is increased.

TABLE 137.

$n/50$  chromic acid ;  $t$  = time in chromic acid ; then sulphited in  
 $n/10$   $\text{Na}_2\text{SO}_3$ , developed in  $n/20$  quinol for 5 minutes.

$t =$		0.	2.	20.	40.	120.
No.	Log E.	$D_1$ .	$D_2$ .	$D_3$ .	$D_4$ .	$D_5$ .
1	1'00	0'098	0'058	—	—	—
2	1'36	0'397	0'0251	0'101	—	—
3	1'575	0'574	0'0500	0'232	0'072	—
4	1'80	0'905	0'908	0'400	0'148	0'050
5	2'14	1'440	1'510	0'603	0'290	0'102
6	2'42	1'923	1'924	0'898	0'421	0'213
7	2'72	2'451	2'401	1'084	0'595	0'325
8	3'01	2'925	2'812	1'303	0'724	0'400
9	3'31	3'360	2'975	1'420	0'860	0'398
	$\gamma$	1'65	1'65	0'77	0'48	0'34
	$\log i =$	1'25	1'25	1'30	1'50	1'80

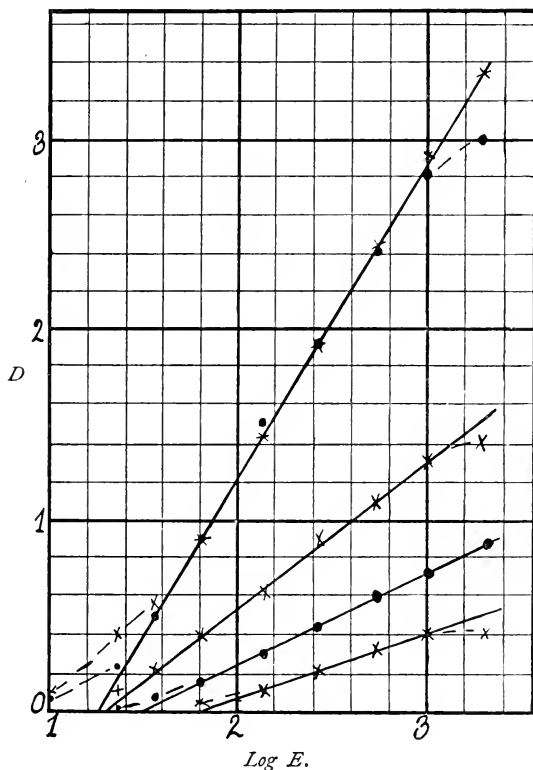
Since  $\gamma$  is proportional to  $\gamma_x$ ,  $K$  being unchanged, it is evident that both  $\gamma_x$  and  $\log i$  are altered, showing a progressive destruction of the latent image.

As to the exact chemical action involved in the destruction of the latent image, we must necessarily remain uncertain. But the phenomena fully agree with the view that a reduction product is formed by light, which forms solid solutions with the unaltered halide. The destruction of this by an oxidising agent would at first follow a similar course to development, *i.e.* the *rate* would be proportional to the *mass* of the photo-product, or that  $\gamma_x$  would be lowered,  $\log i$  remaining the same. But inasmuch as, per grain, a certain minimum quantity, say  $\phi$ , is required to ensure its developability, this limit will be approached sooner by the less exposed grains, so that ultimately  $\log i$  is raised. This effect would be more noticeable with the greater concentrations of the oxidiser, where the reduction potential is greater, and this agrees with the experimental conclusions. It may be noticed in passing that experimenters (*vide* Sterry) have always assumed that any destruction of the latent image must first be evident in the lower exposures, or detail of the image, but evidently the mass law applied to this



points to a different result. We must remember, however, that above a certain limit increase in the photo-halide does not entail increased density, since this depends rather on the number of affected grains. The formation of a solid solution

FIG. 42.—*Destruction of latent image by chromic acid.*



of the photo-product with normal halide would confer upon it greater resisting powers to oxidising agents, just as a trace of silver forming a metallic solution in gold is not dissolved by nitric acid, which will easily dissolve silver in mass. The importance of this point for the photographic process will be repeatedly evident in the sequel.

**On the Effect of Chromic Acid upon the Shape of the Plate Curve.**—It was found that if attempts were made to repeat Mr. Sterry's experiments upon the effect of chromic acid upon the over-exposed portion of the plate-curve, that the results obtained varied enormously, with the concentration of the  $\text{CrO}_3$ , with the time of soaking, with the plates used, and even with the time of development.

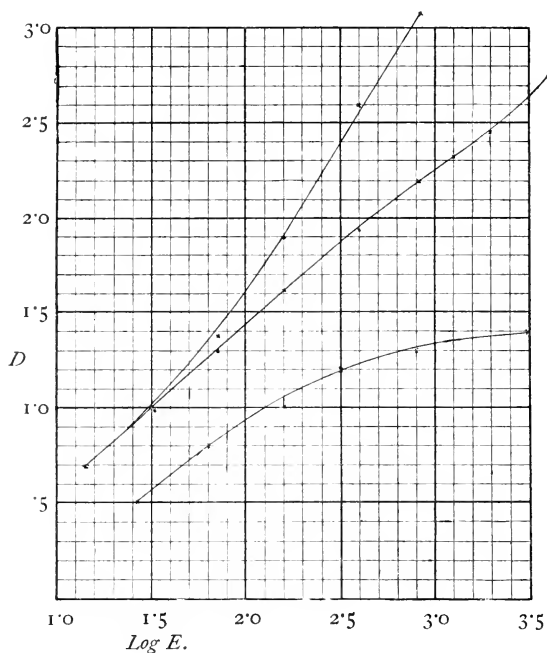


FIG. 43.

Fig. 43, for instance, shows three plates. The curve A belongs to the normal unchromated plate. Plates B and C have been soaked in  $\frac{\text{N}}{100}$   $\text{CrO}_3$  for one minute, and then rinsed, B being developed for a long time, and C for a short.

It is easy, then, to show that if a plate be dipped in chromic acid its curve will sometimes be abnormal, even when developed

to infinity, and that the abnormality will be different at different stages of the development.

Now, if  $\Delta D_{\infty} = \phi(E)$ , we satisfy the first condition; and if, also,  $\Delta \kappa = \phi'(E)$ , we satisfy the second condition.

But in an exposed plate the lower exposures lie near the surface, while the greater exposures penetrate deeper into the film. So that chromic acid, if allowed to act for only a short time, will affect the lower exposures most, and this is just what is experimentally found. So that with short soaking in strong solutions the two conditions given above are fulfilled, the values of  $\phi$  and  $\phi'$  being determined by questions of diffusion.

If a very strong solution be used for a very short time, the whole of the front of the image will be wiped out, but at the back a very strong image will be found, showing that the front image, and consequently the lower exposures, is really attacked first.

Three corollaries follow from this theory—

(1) A plate soaked in dilute chromic acid for a long time will show diminution of  $\gamma_{\infty}$  and  $\kappa$ , but will not give abnormal curves.

This was confirmed on a plate soaked in  $\frac{N}{2000}$   $\text{CrO}_3$  for 30 minutes, which gave perfectly normal curves.

(2) A plate dipped in strong chromic acid for a short time will show very abnormal curves. This was very easily confirmed by momentarily dipping a plate in  $\frac{N}{10}$   $\text{CrO}_3$ .

(3) A plate exposed from the back should give exactly the converse curve to one exposed from the front.

Two plates were exposed, one (A) from the back, the other (B) from the front, chromated in  $\frac{N}{100}$   $\text{CrO}_3$  and developed.

TABLE 138.

Log E.	$D_A$ .	$D_B$ .
2.59	0.710	0.634
2.213	0.472	0.496
1.863	0.300	0.432
1.516	0.201	0.150
1.140	0.072	0.044

Fig. 44 shows that though these numbers are not good, they undoubtedly tend to curve in exactly opposite directions.

*Conclusion.*—We consider, then, that—

(1) Soaking in  $\text{CrO}_3$  produces a fall in  $\kappa$  due to adsorption.

(2) If plates be allowed to stand after soaking, a fall in  $\gamma_\infty$  will result.

(3) This fall in  $\gamma_\infty$  is due to reoxidation of the light reduction product.

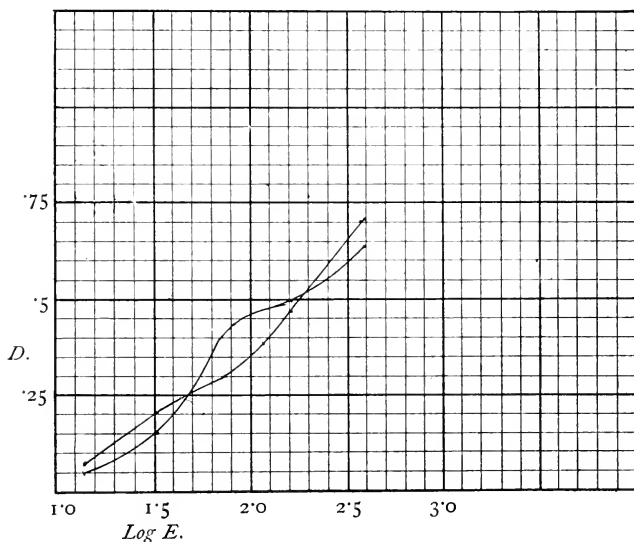


FIG. 44.

(4) The abnormality in curves shown to exist by Mr. Sterry is entirely due to the fact that, owing to questions of diffusion, the lower exposures which are on the surface are affected before the higher ones.

(5) Consequently Mr. Sterry's theory of primary and secondary development is unnecessary.<sup>1</sup>

<sup>1</sup> Mr. Sterry has recently (1907) contributed another paper on the subject to the Royal Photographic Society, and the subject cannot be regarded as settled.

## (b) THE ACTION OF DESENSITISERS.

In July, 1905, we found that if a plate be soaked in a solution of uranium nitrate, it will be found to have largely lost its sensitiveness.<sup>1</sup>

Other nitrates did not show this effect, but other salts of uranium did, so that the action must be ascribed to the metallic ion.

Salts of the following metals were then tried, and gave negative results, though a slight effect was suspected with zinc chloride:—lead, nickel, thorium, chromium, molybdenum, tungstan, ferrous iron, cobalt, silver, zinc, manganese, magnesium, barium, hydrogen (nitric and hydrochloric acids), thallium, platinum.

Stannous salts reduced the silver bromide, platinum bichloride induced fog, while gold chloride produced total reduction on development.

The following salts desensitised the plate:—cupric, ferric, mercuric, and uranic salts.

This desensitising action of copper sulphate is clearly seen in the following experiment.

Two Gem process plates exposed wet for 400 C.M.S. to sector wheel—

(1) Direct.

(2) After soaking in a  $\frac{M}{10}$  solution of copper sulphate for 1 minute.

Developed to  $\gamma_{\infty}$ .

<sup>1</sup> This had been shown previously for other (copper and mercury) salts by Lüppo-Kramer (*Wiss. Arbeiten*), Reiss (*Photo Cent.*, 1902, 16), and Lumière (*Bull. Soc.*, Fr. 1887). Lüppo-Kramer made no quantitative experiments, and concluded that the salt was completely removed.

## Results—

TABLE 139.

Log E.	D <sub>1</sub> .	D <sub>2</sub> .
—	—	0'394
2'60	—	0'104
2'30	—	0'047
2'00	—	—
1'70	2'36	—
1'40	1'55	—
1'10	0'816	—
0'80	0'362	—
0'50	0'078	—

*I.e.* Plate (1) is about 2<sup>7</sup> times as fast as Plate (2), or the plate has been made 64 times as slow by soaking for 1 minute in  $\frac{M}{10}$  CuSO<sub>4</sub>.

In order to investigate this phenomenon, the first question to answer is, "Is the effect produced in development?"

*Experiment.*—Plate exposed and developed in ferrous oxalate containing copper sulphate.

## Results—

TABLE 140.

Log E.	D.
2'00	1'734
1'70	1'258
1'40	0'900
1'10	0'571
0'80	0'251
0'50	0'127

Log  $i$  = 0'80 (from curve), and, from previous experiment without CuSO<sub>4</sub>, log  $i$  = 0'80.

So that copper sulphate in the developer has produced no effect.

Plate soaked 1 minute in  $\frac{M}{10}$  CuSO<sub>4</sub> after exposure, then developed. Result, log  $i$  = 1'18.

Therefore, there is slight action in this manner, the plate having about half the sensitiveness of the unsoaked plate.

A property which the desensitising metals appear to have in common is that they are slight oxidisers. From the previous work on chromic acid, however, we know that oxidisers only slightly affect  $i$ .

This is confirmed by the following experiment :—

Three plates—

- (1) Unbathed (except in water).
- (2) Bathed 1 minute in  $\frac{M}{50}$   $\text{CuSO}_4$  }
- (3) Bathed 1 minute in  $\frac{N}{50}$   $\text{CrO}_3$  } washed.

All exposed and developed together.

Results—

TABLE 141.

Log E.	D <sub>1</sub> .	D <sub>2</sub> .	D <sub>3</sub> .
2'60	2'21	1'020	1'57
2'30	1'768	0'715	1'496
2'00	1'480	0'477	1'340
1'70	1'10	0'260	1'048
1'40	0'764	0'127	0'701
1'10	0'443	—	0'382
0'80	0'208	—	0'180
0'50	0'035	—	—

(Fig. 45.)

This shows the characteristic nature of chromic acid action, and the very different effect of desensitisers.

Another type of action before exposure is that produced by solutions of potassium iodide. But this again is of an entirely different kind, greatly affecting  $\gamma_\infty$ .

Do desensitisers affect  $\gamma_\infty$ ?

*Experiment.*—Four plates taken—1, 2, 3, 4.

1 and 2 soaked 1 minute in  $\frac{M}{50}$   $\text{CuSO}_4$ , washed, and exposed 1600 cms.

3 and 4 washed only, and exposed 200 cms.

1 and 3 developed 4 minutes in  $\frac{M}{10}$  hydrokinone.

2 and 4 developed 8 minutes in  $\frac{M}{10}$  hydrokinone.

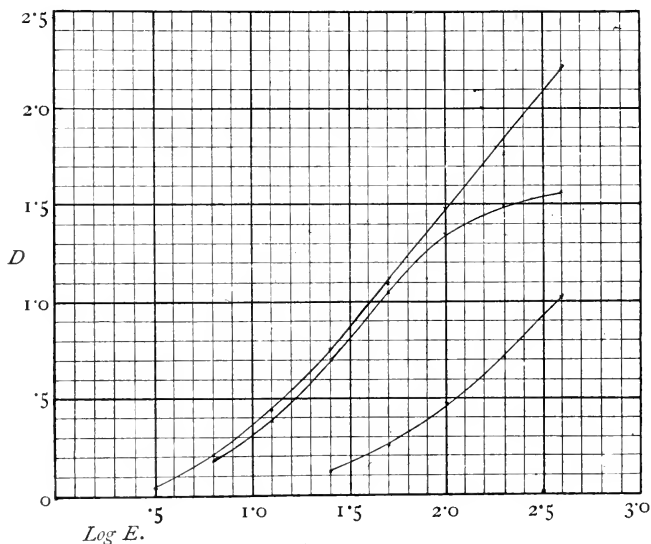


FIG. 45.

*Results—*

TABLE 142.

Log E.	D <sub>1</sub> .	D <sub>2</sub> .	D <sub>3</sub> .	D <sub>4</sub> .
3'20	—	3'29	—	—
2'90	2'34	2'87	—	—
2'60	2'12	2'47	—	—
2'30	1'660	1'71	2'69	—
2'00	1'120	1'24	2'53	—
1'70	0'655	0'719	2'30	3'12
1'40	0'238	0'268	1'96	2'64
1'10	0'072	—	1'462	1'890
0'80	—	—	0'962	1'303
0'50	—	—	0'510	0'764
0'20	—	—	0'192	0'274



From the curves—

Plate.	1.	2.	3.	4.
Log $i$	1.38	1.38	0.45	0.45
$\gamma$	1.77	2.08	1.71	2.20

*Conclusion.*—Neither shape of curve, nor  $\gamma$  (and therefore neither  $\kappa$  nor  $\gamma_{\infty}$ ), are affected by desensitisers.

This conclusion was confirmed by the following experiment.

*Barnet orthochromatic plate.*—Exposed as before—

(1) After washing.

(2) After soaking 1 minute in  $\frac{M}{50}$   $\text{CuSO}_4$  and washing.

Developed 4 minutes in  $\frac{M}{10}$  hydrokinone.

*Results—*

TABLE 143.

Log E.	$D_1$ .	$D_2$ .
3.20	—	2.31
2.90	—	2.07
2.60	—	1.63
2.30	—	1.09
2.00	2.29	0.594
1.70	2.086	0.173
1.40	1.624	—
1.10	1.130	—
0.80	0.710	—
0.50	0.355	—
0.20	0.137	—

(Fig. 46.)

The effect of the concentration of the desensetiser is almost negligible, provided that the plate is allowed to absorb it completely, and that then it is completely washed out again.

This is shown in the two following experiments:—

(a) Three plates soaked 10 minutes.

(1) In  $\frac{M}{200}$   $\text{CuSO}_4$ .

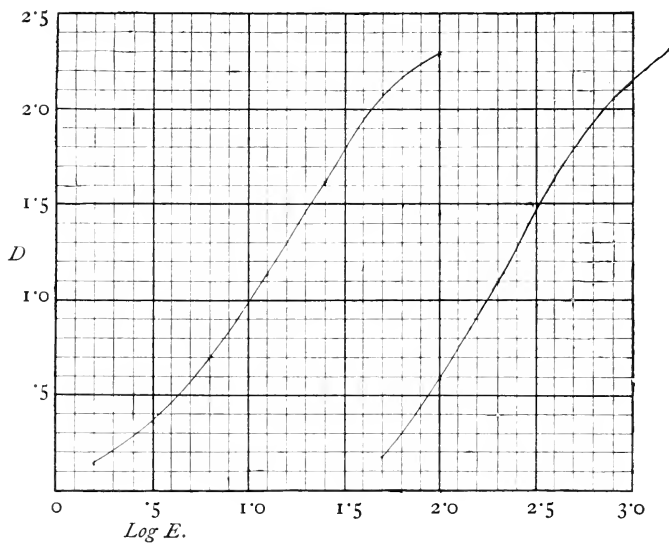
(2) In  $\frac{M}{100}$   $\text{CuSO}_4$ .(3) In  $\frac{M}{50}$   $\text{CuSO}_4$ , and washed completely.

FIG. 46.

TABLE 144.

Log E.	D <sub>1</sub> .	D <sub>2</sub> .	D <sub>3</sub> .
2.90	1.682	1.630	1.828
2.60	1.364	1.446	1.682
2.30	—	1.226	1.348
2.00	0.966	0.852	1.120
1.70	0.680	0.571	0.748
1.40	0.357	0.301	0.406
1.10	0.139	0.113	0.180
0.80	0.057	—	—
Log <i>i</i>	1.05	1.17	1.08

(b) Three plates soaked 10 minutes—

(1) In  $\frac{M}{50}$   $\text{CuSO}_4$ .

(2) In  $\frac{M}{25}$   $\text{CuSO}_4$ .

(3) In  $\frac{M}{10}$   $\text{CuSO}_4$ , and washed completely.

TABLE 145.

Log E.	D <sub>1</sub> .	D <sub>2</sub> .	D <sub>3</sub> .
2.60	—	2.23	2.43
2.30	2.23	2.022	2.022
2.00	1.920	1.890	1.768
1.70	1.685	1.616	1.520
1.40	1.303	—	1.174
1.10	0.852	0.828	0.695
0.80	0.398	0.396	0.319
0.50	0.151	0.131	0.140

*Relative Effects of the Different Metals.*—Plates were soaked in  $\frac{M}{10}$  solutions of the metallic salts, and washed, then exposed and developed.

Plates bathed in {	(1) Water only	(2) $\text{CuSO}_4$	(3) $\text{U}(\text{NO}_3)_2$	(4) $\text{FeCl}_3$	(5) $\text{HgCl}_2$
Log <i>i</i> resultant	1.95	0.502	0.590	1.790	Not found greater than 2

Extent to which plate is made insensitive by—

Cu	U	Fe'''	Hg''
3.6	4.4	69	>100

*Applications of the Properties of Desensitisers.*—In the first place, it is probable that this discovery of the strongly desensitising action of very weak solutions of copper and iron salts may give the clue to some of the peculiar troubles occasionally met with in emulsion-making. It is not unusual for a particular batch of emulsion to suddenly prove itself only

about half the speed which is usually produced. This may sometimes be due to minute traces of iron salts.

Since at the first glance the action of light on bichromated gelatine appeared to be an oxidation reaction, it appeared that it might be possible to catalyse this reaction, and so obtain very sensitive bichromated gelatine. At the L.C.C. School of Photo-Engraving, Bolt Court, we therefore prepared half-tone plates coated with bichromated fish-glue, containing mercuric chloride, and exposed them to an enclosed arc-lamp under a line negative in order to obtain the exposure necessary for printing. The result was entirely negative, practically no increase in sensitiveness resulting from the addition of mercuric chloride to the glue. Probably the *photo-chemical* reaction is not the oxidation of the gelatine but the reduction of the bichromate.<sup>1</sup>

**Theory of the Action of Desensitisers.**—The subsequently described experiments were more particularly devoted to ascertaining the mechanism of the action, and its bearing upon the question of the “latent image.”

In continuing this investigation, we found, in confirmation of the first result, that dipping in  $m/100$   $\text{CuSO}_4$  immediately prior to development had little effect. If, however, the plate was left for several hours in the “desensitiser,” or if after immersion it was rinsed and dried and then left, the latent image was destroyed, showing that the result is only a question of time. Thus of two plates, one was cuprated for five minutes in  $m/100$   $\text{CuSO}_4$ , and both left in a box from Saturday noon to 10 a.m. Tuesday. They were then soaked for three minutes in  $m/100$   $\text{CuSO}_4$ , and developed in  $n/10$  ferrous oxalate.

A, developed nothing but slight fog.

B, full density.

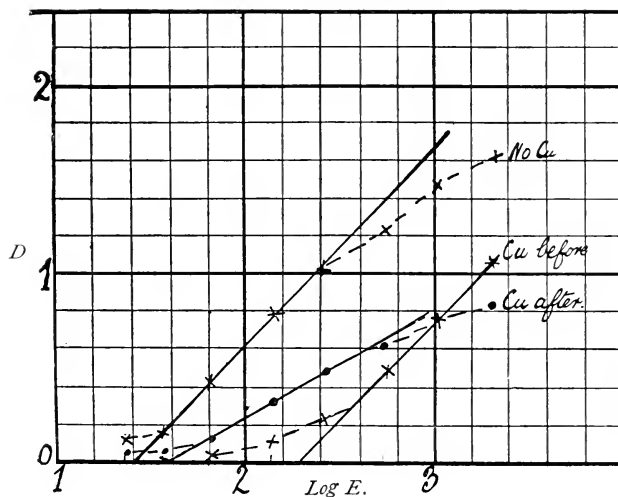
For twelve hours' immersion in  $m/100$   $\text{CuSO}_4$  the following result was obtained :—

<sup>1</sup> Cf. Lumière and Seyewetz, *Bull. Soc. Fran. Phot.*, **X**, 21. 461.

TABLE 146.

(A) no immersion ; (B) immersion ; three minutes' development in  $n/10$  ferrous oxalate.

Log E.	$D_A$ .	$D_B$ .	$D_C$ .
1.36	0.108	0.044	—
1.575	0.155	0.052	0.010
1.80	0.420	0.110	0.027
2.14	0.790	0.313	0.098
2.42	1.002	0.471	0.231
2.72	1.215	0.598	0.464
3.01	1.476	0.743	0.748
3.31	1.624	0.832	1.068

FIG. 47.—Action of  $\text{CuSO}_4$ .

The values for C are for a similar plate, dipped for three minutes in  $m/1000$   $\text{CuSO}_4$ , *before exposure*. It will be seen that the effect is very different from that obtained by a subsequent bath, the lower exposures being relatively more affected, the upper ones not so much.

No Cu.	Cu $n/100$ after.	Cu $n/1000$ before.
$\log i = 1.40$	1.60	2.30
$\gamma = 1.04$	0.54	1.05

Hence, while oxidisers and desensitisers after exposure chiefly affect  $\gamma_{\infty}$ , desensitisers before exposure chiefly affect the inertia, the speed being greatly decreased.

But it appears that ultimately, if a considerable concentration of the desensitiser be used, that  $\gamma_{\infty}$  is also affected. *With organic reducers, such as metol, etc.,  $\gamma$  is lowered.*

TABLE 147.

(A) 3 minutes in metol-quinol, no desensitiser.

(B) „ „ „ „ with 3 minutes in  $m/100$   $\text{CuSO}_4$ .

Log E.	$D_A$ .	$D_B$ .
1.00	0.080	—
1.36	0.282	—
1.575	0.552	—
1.80	0.979	—
2.14	1.616	0.040
2.42	1.840	0.130
2.72	2.106	0.251
3.01	2.270	0.301
3.30	2.312	0.350

The absolute values of the exposures are not given, as the *relative* value of the results is the only question at issue for the theory of the latent image.

It is to be remarked, that if any  $\text{CuSO}_4$  is retained by the film, this would have more action on organic reducers than on ferrous oxalate.

Development with ferrous oxalate being free from the possible action of  $\text{CuSO}_4$ ,  $\text{Fe}_2(\text{SO}_4)_3$  on the developer, as in organic developers, was used exclusively for the remaining experiments.

**The Nature of the Action.**—It is obvious that the peculiar action of desensitisers may be referred to two categories ;

either (a) it alters the sensitiveness of the film prior to exposure, or (b) it acts during exposure by reversing the photo-chemical reaction. Now the first theory would agree with that theory of "ripening" (see later) which supposes the increase of sensitiveness is due to a formation of a slight quantity of the photo-bromide. The second theory requires that a small quantity of the desensitiser be retained by the film, in spite of prolonged washing. The experiment with metol showed that a certain quantity *is* retained, and the following experiments appear to confirm this view, and also to show that the action occurs *during exposure by reversal of the photo-chemical action*, and not by any modification of the sensitive salt.

(a) *Exposure of moist and dry films*: desensitising effect of water. Wratten ordinary plates, exposed three minutes.

TABLE 148.

(A) Soaked 5 minutes in distilled water prior to exposure.

(B) " " " " " development.

Log E.	$D_A$ .	$D_B$ .
1'00	0'023	0'053
1'36	0'084	0'123
1'575	0'140	0'205
1'80	0'286	0'372
2'14	0'650	0'592
2'42	1'020	0'892
2'72	1'387	1'130
3'01	1'734	1'379
3'30	1'940	1'520
log $i$ =	1'60	1'45
$\gamma$ =	1'20	0'92

(See Fig. 48.)

The moist plate has higher  $\gamma$ , *i.e.*  $\gamma_\infty$ , but also higher log  $i$ , *i.e.* the speed is less, a result probably due to slight desensitisation by an impurity. The result agrees with Sterry.<sup>1</sup>

(b) The effect increases with the time of immersion, and it appears that with sufficient immersion very weak solutions have an equal effect with stronger ones.

<sup>1</sup> *Phot. Journ.*, 19, 18, and *ibid.*, 1898, 22, 269.

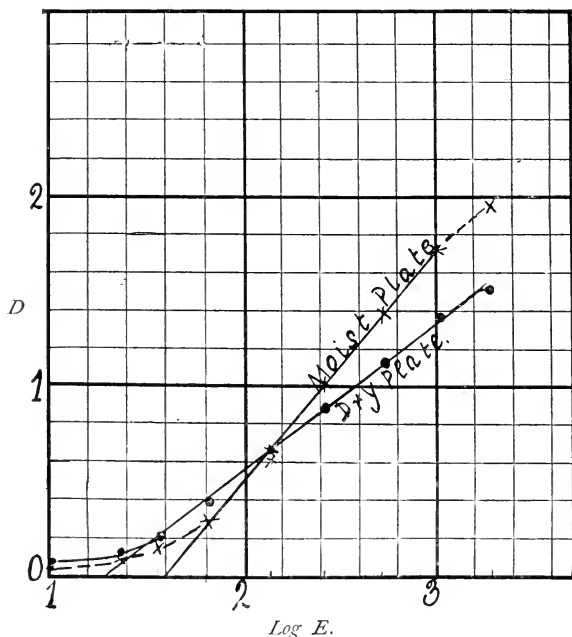
FIG. 48.—*Effect of water on exposure curve.*

TABLE 149.

	<i>n</i> /1000 for 5 mins.	<i>n</i> /10,000 for 5 mins.	<i>n</i> /10,000 for 30 mins.
Log E.	D.	D.	D.
1'00	—	—	—
1'36	—	0'030	—
1'575	—	0'073	—
1'80	—	0'195	0'039
2'14	0'022	0'412	0'071
2'42	0'050	0'600	0'161
2'72	0'092	0'824	0'272
3'01	0'201	1'078	0'564
3'30	0'388	1'364	0'689

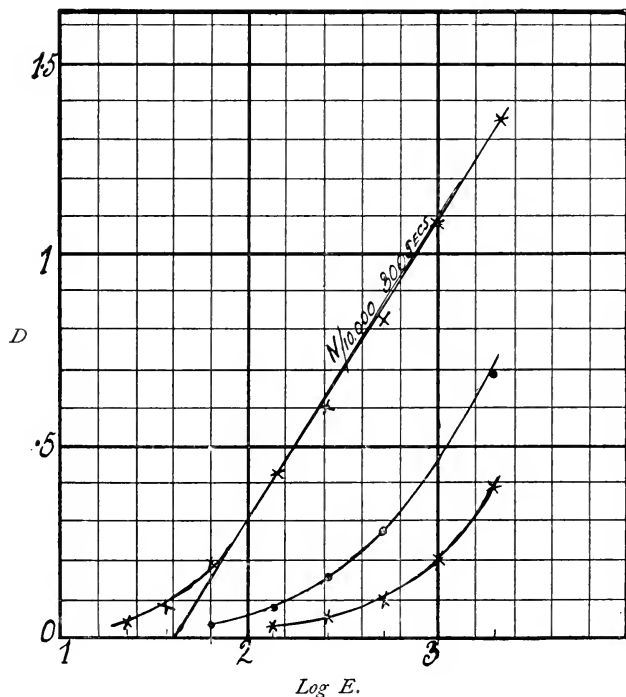
It will be remembered that, with sufficient washing-out, different strengths gave the same effect; it also appears that,



with sufficient soaking and equal washing, the same effect is reached, but that otherwise the effect increases with the concentration.

(c) The effect may be entirely or nearly removed by treating the plate after its immersion in the desensitiser with a substance which destroys this.

FIG. 49.— $\text{CuSO}_4$  at  $N/10,000$  for 5 minutes ;  $N/10,000$  for 30 minutes ;  
 $N/1000$  for 5 minutes.



Thus with copper solutions partial resensitising was obtained with quinine sulphate, and with ferric solutions subsequent treatment with potassium oxalate solution largely compensated for the effect.

TABLE 150.

Wratten instantaneous, 1·0 minute exposure, 3 minutes' development in  $n/10$  ferrous oxalate. (A)  $m/1000$   $\text{CuSO}_4$ , 5 minutes; (B)  $m/1000$   $\text{CuSO}_4$ , 5 minutes, followed by 5 minutes in saturated quinine sulphate in  $n/50$   $\text{H}_2\text{SO}_4$ ; (C) no  $\text{CuSO}_4$  or quinine.

Log E.	$D_C$ .	$D_B$ .	$D_A$ .
1·00	0·020	0·020	—
1·36	0·108	0·088	—
1·575	0·155	0·145	0·010
1·80	0·420	0·375	0·027
2·14	0·790	0·562	0·098
2·42	1·002	0·860	0·231
2·72	1·215	1·058	0·464
3·01	1·476	1·490	0·748
3·30	1·624	1·660	1·068

Evidently the quinine largely prevents the action. The next examples show the "resensitising" action of quinine with copper, and of oxalate with  $n/1000$   $\text{Fe}_2(\text{SO}_4)_3$ . From the latter it appears that the effect is due to ferric ions, the ferric complex not being so effective.

TABLE 151.

	No desensitiser.	$n/1000$ Cu.	+ quinine.	$n/5000$ Fe.	+ oxalate.
Log E.	$D_1$ .	$D_2$ .	$D_3$ .	$D_4$ .	$D_5$ .
1·00	0·023	—	—	—	—
1·36	0·084	—	—	—	0·047
1·575	0·140	—	—	0·020	0·066
1·80	0·286	—	0·043	0·051	0·109
2·14	0·650	0·022	0·078	0·086	0·309
2·42	1·020	0·050	0·187	0·251	0·616
2·72	1·387	0·092	0·421	0·460	0·936
3·01	1·734	0·201	0·719	0·692	1·270
3·30	1·940	0·388	0·988	0·936	1·616

From all these results it appears justifiable to conclude that a definite quantity of the metallic salt is irreversibly absorbed by the silver halide, and that this subsequently counteracts the photo-chemical action during exposure. It is probable that something of the nature of a solid solution is formed, the

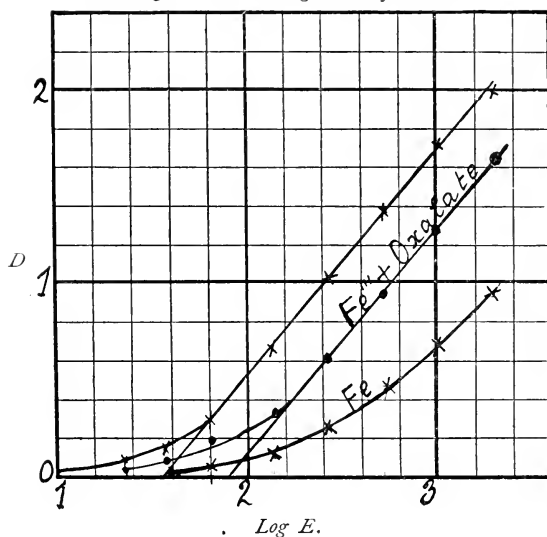
maximum effect with any salt being the quantity which forms a saturated solution in the halide.

**The Mechanism of Desensitising.**—One striking point about this action is that it is noticeable with extremely small quantities of the metallic salts which possess an action. Thus in two hours' time the following effect was obtained with  $m/100,000$   $\text{CuSO}_4$  :—

TABLE 152.

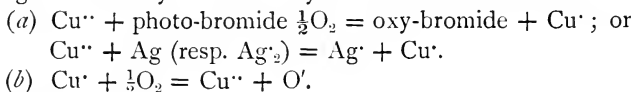
Log E.	$D_A$ .	$D_B$ .
1.00	0.023	—
1.36	0.084	—
1.575	0.140	0.023
1.80	0.286	0.080
2.14	0.650	0.218
2.42	1.020	0.351
2.72	1.387	0.525
3.01	1.734	0.900
3.30	1.940	1.182
$\log i =$	1.60	2.25
$\gamma =$	1.20	1.14

FIG. 50.—Resensitising action of oxalate.



The desensitising action of water is probably to be attributed to a slight amount of some foreign substance. Moreover, if a plate be exposed, containing  $\text{CuSO}_4$ , so that it develops a full density, and then left, the image again disappears, so that a very small amount of the desensitiser is able to continually destroy the latent image. The action may be described as catalytic, the metallic ions effective all being known to act as catalysts in oxidation processes. Thus Titoff<sup>1</sup> has shown that copper has an extraordinary accelerating effect on the oxidation of sodium sulphite by atmospheric or dissolved oxygen, even one gram-molecule in a milliard liters having a definite effect. Certain substances, such as mannite, stannous salts, quinine, etc., inhibit the positive catalysis, and hence act as negative catalysts.<sup>2</sup> There are two actions, an acceleration of oxidation by the copper (respectively mercury, uranium, iron) salt, and the destruction of this by union with the negative catalyst. Thus for the desensitising action, quinine, metol, and oxalates were found to act as negative catalysts; benzaldehyde and stannous salts also acted as resensitisers, but fogged the plate. In agreement with Titoff, much larger quantities of the negative catalyst (quinine, etc.) were required to annul the action than corresponded to the copper concentration.

Probably the catalysis is to be referred to pseudo-catalysis or Übertragungs-catalyse (Wagner, Ostwald), since we may assume that the copper takes a definite part in the chemical change. Probably we have a cycle of actions of the form—



the reformed copper (or ferric, etc.) salt again taking part in the action. During exposure, we may assume that the halogen is restored to the reduction-product, and normal halide reformed. The effect would be less after exposure, since the photo-bromide, by forming a solid solution with unaltered halide, acquires greater resisting power.

<sup>1</sup> *Zeit. phys. Chem.*, 1903, **45**, 641.

<sup>2</sup> See also Bigelow, *Zeit. phys. Chem.*, 1898, **27**, 585; and S. W. Young, *Journ. Am. Chem. Soc.*, 1901, **23**, 119.

It appeared probable on this view that the *intermittency failure*, if due to a reverse action, might be increased if a desensitiser were present. The following experiments are for 50 revolutions per minute and 500 revolutions per minute, one set without desensitiser, the other with  $m/2000 \text{ Fe}_2(\text{SO}_4)_3$ .

TABLE 153.

No.	Log E.	No desensitiser.			$m/2000 \text{ Fe}'''$ .		
		$D_{\text{fast.}}$	$D_{\text{slow.}}$	Ratio.	$D_{\text{fast.}}$	$D_{\text{slow.}}$	Ratio.
1	1'00	—	—	—	—	—	—
2	1'36	0'018	0'020	(1'01)	—	—	—
3	1'575	0'071	0'092	1'29	—	0'027	—
4	1'80	0'137	0'179	1'30	0'020	0'050	2'50
5	2'14	0'272	0'341	1'25	0'076	0'184	2'42
6	2'42	0'466	0'530	1'14	0'244	0'350	1'43
7	2'72	0'710	0'748	1'06	0'481	0'600	1'25
8	3'01	0'892	0'979	1'08	0'748	0'975	1'30
9	3'30	1'124	1'174	1'04	0'970	1'094	1'13

It will be seen that there seems to be an increase in the intermittency failure when a *desensitiser* is present, so that from all the experimental evidence for the destruction of the latent image hitherto brought forward, there seems to be little doubt that *the developable condition is due to a chemical change* in a small portion of the halide, and that this change is, *chemically speaking, a reduction*. The foregoing, however, throws but little light on the exact nature of the reduction product, leaving unsettled the question as to whether it consist of metallic silver or subhalide. But the general behaviour of the latent photographic image to oxidising agents, and in particular to nitric acid, favours the latter view.

**Action of Nitric Acid.**—Nitric acid applied to gelatino-bromide plates induces fog, and at high concentrations destroys the gelatin, so that experiments with these are of little value. For this reason collodion-emulsion is preferable, and with this the question has recently been thoroughly investigated by Dr. J. M. Eder.<sup>1</sup> Contradictions as to whether nitric acid destroyed the

<sup>1</sup> *Sitz. ber. Wien. Akad.*, 1905, **114**. 2A. Juli; *Zeit. wiss. Phot.*, 1905, **III**. 329.

latent image or not are shown by Eder to be due to insufficient consideration of the quantities of light acting. He finds that concentrated nitric acid S.G. 1.40 at 15° destroys the latent image for physical development up to about 15–20 times the first developable impression in about 5 minutes, to 40 times the Schwellenwert in about 10 minutes, while the remainder is much weakened and the gradation ( $\gamma_x$ ) lowered. The visible blackening in light is not destroyed by the acid, but metallic silver is dissolved in a few minutes. Plates exposed with silver nitrate in the film are more sensitive; nitric acid present lowers the sensitiveness, but an image is ultimately formed. Similar results were obtained for chemical development, *i.e.* reduction of the silver *halide* by an alkaline developer. He concludes that there exist different kinds of sub-bromide which behave alike to chemical and physical development, but show very different resisting powers to nitric acid. In any case, the reduction-product for considerable (normal) exposure, even the less resisting, withstands nitric acid far better than metallic silver.

To the conception of various sub-bromides, apart from objections from the theory of chemical combination (valency), it may be pointed out that no other evidence that they exist has been brought forward. The behaviour of the photo-bromide seems to be sufficiently explainable on the following considerations:—

(a) The half-halide forms mixtures or solid solutions in all proportions with normal halide (Baur, Gunther, Lea).

(b) In consequence of the thickness of the film and absorption of light (*vide* p. 210), there exist layers of halide grains with varying amounts per grain of photo-bromide. If  $n$  grains reduced to metallic silver be required for a first visible impression (Schwellenwert), this will be shifted by the oxidation of the latent image, progressively with time and concentration, but as the amount of half-halide is lessened, its concentration in the unaltered halide falls, and the potential of the oxidising solution necessary to destroy it must be raised. Hence in the more richly exposed portions there will still be left sufficient grains with a minimum of half-halide sufficient to give a considerable density on development.

In considering the action of oxidising agents, care must always be taken to distinguish the reduction in the *velocity* of development brought about by adsorbed oxidizer (p. 238). This does not seem to have been noticed heretofore.

**The Developable Image after Fixation.**—Another important argument in favour of the chemical reduction theory is the existence of an image capable of physical development (silver nitrate + acid reducer) after fixation or solution and removal of the silver halide. According to Eder, fixation removes any image-forming remnant up to about 4–10 times the Schwellenwert for ordinary development. The chemical nature of this remainder cannot be determined by any quantitative analysis, since the mass is extremely minute. Microscopic investigation of fixed plates reveals nothing, and the results of an investigation by the ultra-microscopic method of Zsigmondy and Siedentopf are indefinite. Hence it is only possible to express opinions based on its behaviour to reagents. The attraction for nascent silver which permits of visible development says nothing, since, as has already been emphasized, the most varied substances may act as “germs” to a supersaturated solution. Lüppo-Kramer<sup>1</sup> considered that it consisted of metallic silver, its behaviour to reagents being conformable. Thus treatment with bromine is said to remove the developability, but this is restored by re-exposure. Reagents which dissolve silver destroy it. But its behaviour to nitric acid is indecisive.

Precht considered that the remnant consisted of silver sulphide, but since a remnant may be left when ammonia or cyanide or other non-sulphurous fixing agents are employed, this appears improbable. Sterry,<sup>2</sup> following Hardwich,<sup>3</sup> considered that the image developable after fixation was a product of the decomposed silver halide with organic substratum, but Eder points out that as pure silver iodide in pure collodion behaves similarly, this does not seem necessary; moreover, collodio-bromide in the presence of concentrated nitric acid or silver nitrate shows the same phenomenon, which renders

<sup>1</sup> *Phot. Corr.*, 1903, 229.

<sup>2</sup> *Phot. Journ.*, 1898, **22**, 264; *Eder's Jahrbuch*, 1899, 290.

<sup>3</sup> *Phot. Chem.*, 6th ed., 36.

the formation of the hypothetical organic compound highly improbable.

As to its behaviour to nitric acid, Eder concludes that the primary fixed image is destroyed for short exposures by this treatment, but only weakened for long exposures. While the latent image before fixation resists nitric acid far better than silver, the primary fixed latent image behaves rather as a mixture of metallic silver and photo-bromide. Apparently part of the subhalide is converted to metallic silver by the thiosulphate.

**Other Chemical Actions of the Latent Image.**—Schaum found that neither silver nitrate nor platinum solutions were reduced to the metallic condition by the latent image, and hence concluded that its potential must differ considerably from metallic silver. But Homolka<sup>1</sup> found that the latent image could be developed with a plain solution of gold chloride. This was confirmed as follows. A plate was treated for 12 hours with  $m/100$   $\text{AuCl}_3$ , and a reddish-brown image of metallic gold was formed, which ceased to gain strength after a while. The densities were measured, with the following results:—

TABLE 154.

Log E.	D.
2.06	0.018
2.41	0.060
2.79	0.148
3.13	0.213
3.30	0.265
3.46	0.297
3.80	0.350

$$\log i = 2.1.$$

$$\gamma_{\infty} = 0.021.$$

The value of  $\log i$  for normal development was 1.96, so the Schwellenwert and inertia are much raised. The image was light yellow by transmitted light, red by reflected.

This action might possibly be due to a form of so-called physical development. We have seen already that gelatin

<sup>1</sup> *Eder's Jahrbuch*, 1905.



reduces gold to the metallic state, and this would then, just like silver from a supersaturated solution, be deposited on the latent image. An attempt to repeat the experiment with gelatin-free silver bromide gave uncertain results, but traces of a visible image were formed on the highest exposures, so apparently the latent image there can bring about the chemical change  $\text{Au}''' \rightarrow \text{Au}$ . It is possible that more definite information as to the potential of the latent image may be obtained by further experiments on these lines with gold chloride.

**The Process of Ripening.**—Before attempting to sum up the series of actions in the photographic process, it is necessary to say a few words as to the nature of "ripening," and on the preliminary action in exposure to any chemical reaction. Ripening is the name given technically to various treatments which increase the sensitiveness of silver halide emulsions. We may notice the following points.<sup>1</sup>

The character of the gelatin is of great importance. Such characteristics as the melting-point, solidification point (neither sharply defined), viscosity in aqueous solution, absorption for water, reducing power on ammoniacal silver nitrate, have all been more or less investigated,<sup>2</sup> but no systematic inquiry as to their relation to the sensitiveness numerically expressed has yet been made. In addition, experiments have been made with other colloids.<sup>3</sup>

Ripening may be brought about either in the cold by certain additions to the emulsion, especially ammonia, or by digestion at a moderately high temperature. The addition of various substances to the emulsion has been the subject of many experiments,<sup>4</sup> but with little result of systematic value. Generally silver solvents facilitate ripening. Oxidising agents retard it, but this has been dealt with under desensitisers, while reducing agents are said to have a favourable influence. But this may be merely due to a destruction of a desensitiser.

<sup>1</sup> Cf. *Eder's Hdbuch.*, III. 1890.

<sup>2</sup> Eder, *loc. cit.*; Lohse, *Eder's Hdbuch.*, III. 1890, 25; Abney, *Eder's Jahrbuch*, 1887, 299.

<sup>3</sup> Agar-agar, by W. Rebjkow, *Eder's Jahrbuch*, 1892, 386; Silicic acid, by L. de Bruyn, *Chem. Centr.*, II. 1900, 889.

<sup>4</sup> V. Bellach, *Struktur d. Phot. Neg.*, 17.

The most noticeable alteration brought about by ripening is the increase in the size of the halide particles,<sup>1</sup> a process identical with the change brought about in fine-grained precipitates. The smaller particles have a greater solubility than the larger; they go into solution, which becomes supersaturated with respect to the larger particles, so that these increase further in size.<sup>2</sup> Little explanation has been given as to how this influences the sensitiveness, but one doubtless consists in the fact already emphasised, that the *grain* is the limiting aggregate in development, while another is probably the alteration in the opacity and reflecting power to light. Hurter and Driffeld<sup>3</sup> have shown that the "speed" or sensitiveness of a plat depend largely on these physical factors.

A second change postulated as increasing the sensitiveness in ripening is the formation of a small amount of light-reduction product (photo-halide) by the reducing power of gelatin at higher temperatures.<sup>4</sup> But this does not account for the process of ripening in the cold with ammonia, and also (if confirmed) the greater sensitiveness of silicic acid emulsions. Moreover, Schaum and Braun found that gelatin-free halide was susceptible of a certain amount of ripening. However, over-ripened emulsions certainly tend to fog. A definite crystallisation of the silver halide occurs on prolonged ripening (*vide* p. 71), and some have sought an explanation in this, or generally in a "modification" of the halide.<sup>5</sup> But the transition of bodies from a labile form (as amorphous halide) to a stable one is always accompanied by a diminution of the free energy, so that from this cause the emulsion would become not more but less sensitive.<sup>6</sup>

There is no doubt that the principal factor in the increased sensitiveness is the greater absorption for light or opacity. But

<sup>1</sup> See p. 70; and Bellach, *op. cit.*, p. 69.

<sup>2</sup> Cf. Ostwald, *Zeit. phys. Chem.*, **34**, 495, 1900.

<sup>3</sup> *Phot. Journ.*, 1898, **22**.

<sup>4</sup> Abegg, *Arch. wiss. Phot.*, 1899, **I**, 15; Guébhardt, *Compt. rend.*, 1898, **126**, 40; Stolze, *Eder's Jahrbuch*, 1890, 306.

<sup>5</sup> Lüppo-Kramer, *Wiss. Arb.*

<sup>6</sup> Cf. K. Schaum, *Arch. wiss. Phot.*, 1900, **II**, 9.

how is this brought about? Mere increase in the size of the grain for the same mass of material will not do this. As a hypothesis we wish to put forward a suggestion not hitherto applied to this process. Attention has already been drawn to Quincke's researches on the nature of silver halide emulsions, and we may regard these as a most intimate mixture of gelatin and halide, partly a solution. Certainly the gelatin cannot be completely removed by mechanical means, such as centrifugalising. Now, the vibrations of light are considered to be of electro-magnetic nature, and the absorption of light as conditioned by resonance, just as the absorption of Hertzian waves, which can be experimentally studied as a resonance phenomenon. Every electro-magnetic resonance, every preformed electro-magnetic period, is conditioned not only by the electric and magnetic properties of the resonator and *its surrounding medium, but also necessarily by their spatial distribution*.<sup>1</sup> In fact, the vibration period increases with the spatial extension of the resonator, with the closeness of their packing, and with the dielectric constant of the medium. According to Planck,<sup>2</sup> the magnitude of the absorption is proportional to the intensity of the exciting vibrations proper to the resonator, to its logarithmic decrement, and to the cube of the light velocity; and inversely as the frequency. Now, according to the researches of R. Zsgimondy by the ultra-microscopic method,<sup>3</sup> gelatin consists of a homogeneous mass containing aggregates, the proportion being variable, and influenced by the state of the gelatin. In a gelatin emulsion these "knots" or aggregates would be naturally associated with the halide, giving their form and distribution to the same. They may be considered as forming the resonators, or groups of systems of resonators postulated above, and this offers an explanation of one function of gelatin as a sensitiser and the influence of cooking in ripening. To the formation of these aggregates is probably due the slow increase in viscosity on "cooking" gelatin, noted

<sup>1</sup> Cf. Luther, *Die Aufgaben d. Photochemie*, *Zeit. wiss. Phot.*, 1905, III. 264.

<sup>2</sup> *Ann. d. Phys.*, 1900, I. 92.

<sup>3</sup> *Zeit. Elektrochem.*, 1902, 8. 686.

by Schröder. It is evident that there is a wide field of research for the correlation of the sensitiveness with the properties of gelatin and the alteration of these. The event of a possible preliminary reduction, and even the absorbent capacity of gelatin for free halogen (Vogel's definition of a "sensitiser" was a substance absorbing free halogen), must be considered as secondary to the physical process indicated above.

**The Beginning of Chemical Change and the Electron Theory.**—Our conceptions of the inner mechanism of chemical change have been greatly modified in recent years by the advent of the electron theory, founded on the phenomena of electric discharge through gases and of radio-activity. In particular we may hope that a unifying conception in photo-chemistry may be obtained from this theory. Naturally it is not intended to discuss the general bearing of the theory on photo-chemistry, but it appears desirable to briefly refer to its connection with the photographic process. Attention has been drawn to this by Dr. Joly.<sup>1</sup> To begin with, even a certain degree of photographic action is possible at extremely low temperatures. According to Dewar, the photographic effect is reduced to about 20 per cent. at  $-180^{\circ}$  C., and 10 per cent. at  $-252^{\circ}$  C. It is maintained by some that this disposes of any possibility of the latent image being due to chemical action; this question has been dealt with by Luggin.<sup>2</sup> He points out that the temperature coefficient of photo-chemical reactions is always small, and we have no reason to deny a definite, if immeasurably small, halogen pressure even at these low temperatures.

**The Photo-electric Effect.**—Not only do gases traversed by ultraviolet light become conductors, but a series of investigations<sup>3</sup> has shown that a large number of both solid and liquid substances lose a negative charge under ultraviolet light, *i.e.* if negatively charged, they rapidly lose the charge, while if

<sup>1</sup> Address to the Phot. Convention, 1905. *Brit. Journ. of Phot.*, 1905, **52**, 551.

<sup>2</sup> *Zeit. phys. Chem.*, *loc. cit.*

<sup>3</sup> Hallwachs, *Wied. Ann.*, **33**, 308; Stoletow, *Compt. Rend.*, **106**, 1149 and 1593, **107**, 91, **108**, 1241; Elster and Geitel, *Wied. Ann.*, **57**, 24 and **38**, 497, also in **51**, **52**, **53**, **55**.

neutral they acquire a positive charge. The sensitiveness of the effect depends upon the absorption, there being always strong absorption with a marked photo-electric effect. Further, the photo-electric effect is greatest for the spectral region which is chiefly absorbed. The silver halides are highly photo-electric, as are many dyes used as sensitisers.

The phenomena admit of explanation on the view that the incident light—by reason of the electric component in the light-wave—sets free the electron or negative corpuscle. At a bounding surface these, on projection into the gas, ionise the gas molecules, and are carried away by diffusion and convection, or, if in an electric field, move in accordance so that the gas conducts.

But there is another photo-electric effect requiring mention. Many substances, and in especial the silver halides, copper oxide, metallic silver, if immersed in an electrolyte and used as two poles, show a difference of potential if one pole be illuminated and the other kept in darkness.<sup>1</sup> This has been quantitatively studied for silver plates in various electrolytes by M. Wilderman.<sup>2</sup> He shows that the solution pressure of the exposed plate increases. The total E.M.F. produced by light is one due to light at constant temperature (increased solution pressure), and a thermo-E.M.F. caused by heating of one plate. Both are directly proportional to the light intensity. There is an induction and deduction period for constant reversible cells; the

action is described by the law  $\frac{d\pi}{dt} = C(\pi'_0 - \pi)(\pi - \pi_0 + K)$ , *i.e.* the speed with which the system approaches its new state of equilibrium, characterised by the E.M.F.  $\pi'_0$ , is given by its distance from this at any time  $(\pi'_0 - \pi)$ , where  $\pi$  is the E.M.F. at time  $t$ , and the variation hitherto produced  $(\pi - \pi_0 + K)$ , where  $\pi_0$  = E.M.F. in dark, and  $K$  is an instability constant. The E.M.F. gives the true measure of the amount of silver salt decomposed by light.

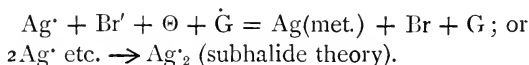
<sup>1</sup> Minchin, *Phil. Mag.*, **31**, 207, 1891; J. C. Bose, *Proc. Roy. Soc.*, 1902; Hankel, *Ber. d. Sachs. Ges. d. Wiss.*, 1875, **27**, 298; Rigollet, *Ann. de Chim. Phys.* 1891, (2), 27.

<sup>2</sup> *Roy. Soc. Proc.*, 1904, **74**, 369.

Scholl<sup>1</sup> finds that silver iodide immersed in aqueous salt solution and exposed to light undergoes a species of dissociation which produces the ions of AgI (cf. Wilderman), and probably also negative electrons. These latter are much more mobile than the electrolytic ions in solid AgI, and impart metallic conductivity to this. He also considers that a new substance is formed from the silver iodide, unaccompanied, however, by the liberation or absorption of free iodine, but this substance is photo-electrically unstable. Arrhenius has formerly shown<sup>2</sup> that the conductivity of the silver halides is increased in light.

Collecting these results, we must agree that the electron is set free not only at the surface, but throughout the substance, so long as the light intensity is sufficient. This inter-atomic event may be regarded as the primary change. Joly considers that the latent image is built up of ionised atoms or molecules, the result of the photo-electric effect on the halide, and upon these ionised molecules the chemical effects of the developer are subsequently developed. But it remains to be explained why the potential differences should remain so long without discharging, and also why the latent image is destroyed by oxidising agents.

Rather does it seem that the primary chemical event is the liberation of the electron, the increased ionisation brings about a chemical change (if temperature and other conditions are favourable), and the chemical product is, when below the threshold of perception, the so-called latent image. In the photographic process, for example, we have—



G is a molecule which becomes positively charged to  $\dot{\text{G}}$  (molion) by the photo-electric process.

Many of the phenomena of photographic induction, reciprocity failures, and so forth (Clayden effect), are probably,

<sup>1</sup> *Ann. dir. Phys.*, 1903 [iv.], 16. 193-237, 417-463.

<sup>2</sup> *Wien. Ber.*, 1887, 96.

after more experimentation, susceptible of explanation by this theory. For it may be noted that, to ionise a molecule, work equal to the potential ionic energy  $e_i = e_e - e_a$  must be afforded. That is,  $\alpha_i$ , the work of ionisation, must = or  $> e_i$ . This ionic energy depends on the ionic pair, the nature of the medium, and the absolute temperature. As it possesses a certain value, ionisation is only possible if the intensity be above this value.<sup>1</sup> The action of other ions than free electrons on the silver halides has been discussed by K. Schaum.<sup>2</sup> A few other details will be noted in the summary, but we must specially refer to colour sensitisers.

**Colour Sensitisers.**—As is well known, the addition (in emulsification or by subsequent bathing) of certain dyes confers sensitiveness on silver halides for the region for which these absorb light (shifted by some  $20 \mu\mu$ ). The investigations of Eder and others (Part III. Chap. III. p. 332) show that an efficient sensitiser must actually dye the silver halide grain, and not merely stain the plate. But the latent image formed behaves to chemical reagents (oxidisers, Eder; desensitisers, p. 256) precisely as the normal or blue violet image. Joly has pointed out that these dyes are photo-electric, and, from the parallelism between absorption and photo-electric effect, we have here the setting free of electrons from the sensitiser, which then act on the silver halide in the manner noted above.

The photographic process simplified consists in the passage of ionic silver to metallic, possibly with the intermediate stage of the subhalide. We have now worked backwards through the stages of the process from exposure to finished negative, and it seems convenient to summarise these. Naturally it has been impossible to deal adequately with any stage, but the summary will serve to further emphasise the complexity of the process and the number of factors operating.

(1) Ripening, due to (a) formation of resonating systems, (b) formation of reduction product.

*Function of gelatin* : forms resonators and assists reduction.

<sup>1</sup> Cf. Stark, *Die Elektrizität in Gasen*. Leipzig, J. A. Barth.

<sup>2</sup> *Zeit. wiss. Phot.*, 1904, II. 205.

(2) Absorption of light, electrons set free which ionise the halide and surrounding gas.

*Function of gelatin*: high dielectric constant, photo-electric, conserves electrons.

*Function of gas*: according as it removes electrons or not, may diminish sensitiveness.

Electrons may be emitted either (*a*) from halide, or (*b*) from sensitiser.

(3) Ionisation leads to chemical reduction; electrolytically dissociated halide becomes discharged by interaction with electrons and positive atom- or mol-ions (cf. Scholl).

*Function of gelatin*: absorbs free halogen, preventing this from converting the reduction product on cessation of light.

The reduction probably results in the formation of half-halide ( $\text{Ag}_2\text{X}$ ) in solid solution in the remaining halide. The reaction is reversible, and, where the halogen is not removed, reaches ultimately an equilibrium, whereby each light intensity is balanced by a definite halogen pressure.

*Destruction of latent image*—

(*a*) Free halogen during and after exposure.

(*b*) Desensitisers during exposure; cyclic action, with oxygen playing a part.

(*c*) Oxidisers after exposure; reoxidation, probably with halogen in gelatin.

(*d*) Reversal—(*a*) halogen reconverts subhalide, ( *$\beta$* ) halogen (absorbed) oxidises developer.

It should also be noted that ionised oxygen formed by the photo-electric effect may be considered as helping reversal,<sup>1</sup> but its tendency to ionise not being great,<sup>2</sup> at another stage it may increase the photographic effect.

(4) Subhalide reduced to metallic silver by developer; formation of silver germ and continued reduction according to

<sup>1</sup> On "active" oxygen and ionisation, see W. P. Jorissen, *Chem. Weekblad*, **I**, 337.

<sup>2</sup> Wulf, *Ann. Phys.*, **9**, 946.



silver germ theory of development (see Chaps. III. and V.). The process may be divided into two stages—

- ( $\alpha$ ) Formation of silver “germ,” chiefly dependent on chemical velocities : *induction period*.
- ( $\beta$ ) Deposition on silver germ, chiefly dependent on diffusion processes : *steady state*.

It should be noted, as to the function of subhalide, that if a mean oxidation stage exist, which under the experimental conditions decomposes spontaneously to the two extremes, it is a stronger oxidiser than the higher, and a stronger reducer than the lower stage.<sup>1</sup> If subhalide occur as an intermediary product in development (a view supported by certain phenomena), then the acceleration of reduction is explainable on the theory of accumulation of the intermediate stage.

*Function of gelatin* : acts as a filter against “germs” ; in the absence of germs for development, colloidal silver may be formed, which is coagulated chiefly on the surface, forming dichroic fog.

- (5) Fixation or removal of remaining AgBr (see Chap. V.).

<sup>1</sup> Luther, *Zeit. phys. Chem.*, **34**. 488, and **36**. 385.

# PART III

## *THE SENSITOMETRY OF PHOTOGRAPHIC PLATES*

### INTRODUCTORY

THERE are two reasons which may be urged for the development of accurate systems of sensitometry. In the first place, the photographic plate can only become a quantitative means of research if the relation between light acting, developer acting, and effect produced, be known; and, in the second place, the development of the plate-making industry must be associated with more accurate knowledge of the properties of its products. To take the second reason first, in the early days of dry-plate manufacture the testing methods employed were of the crudest nature, and consequently many entirely erroneous methods of manufacture were persisted in. The work of Messrs. Hurter and Driffield was the means of introducing into the factories a more scientific and accurate method of testing, and resulted in a great improvement in the higher-speed plates. It is probable that, if the true relation between density-giving power and "speed" in emulsions were better understood, another considerable improvement in the quality of plates would ensue. Moreover, in view of the development of colour-printing which is resulting from the replacement of lithography by three-colour, half-tone processes, an investigation of the properties of colour-sensitised plates becomes of great importance.

The use of photographic plates as instruments of quantitative research presents an entirely different aspect, and requires

somewhat different conditions to be fulfilled. For commercial purposes a final accuracy of about 5 per cent. is as good as can be desired ; but for scientific purposes no accuracy can be too great. It is clear that if a given mass of silver on a plate, under fixed conditions of development, is associated with a known amount of radiant energy of given wave-length, then we can measure the amount of any incident energy by the mass of silver produced under our fixed conditions.

The applications of this are too manifold to detail. One of the few applications already in use is in star photometry. If, as seems probable, the intensity of line spectra becomes of importance, then the photographic plate would be the simplest quantitative instrument of research.

In connection with the following section, the investigation given in the second part, Chap. VI. pp. 214-222, dealing with the departures from the reciprocity law, should be carefully considered, as these have an important bearing both on sensitometry and the quantitative use of the photographic plate in research. The following section deals with the sensitometry of ordinary plates, the effect of wave-length on gradation, and the sensitometry of ortho-chromatic plates. Some portion, especially of the first chapter dealing with general sensitometry, is to some extent a repetition of questions dealt with in development. It is desirable, however, to enforce the sensitometric import of those results, so that in some cases special examples are retained.

## CHAPTER I

### THE SENSITOMETRY OF PHOTOGRAPHIC PLATES

#### HISTORICAL INTRODUCTION

DURING the rise of photographic industry and the development of great factories devoted to the accurate and regular preparation of dry plates, many attempts have been made to obtain an easy and accurate method of estimating the working value of the plates employed.

The earliest method of comparing the sensitiveness of gelatine dry plates seems to have been the description of them as of so many times the sensitiveness of wet plates, a method which still survives in the names of some well-known commercial plates. This exceedingly crude measurement soon gave place to the use of what were known as "sensitometers," these sensitometers being composed of various "blacknesses" of glass with numbers impressed, and the sensitiveness of the plate was said to be the last number visible after the exposure of the plate to a standard light and its subsequent development.

Early instruments of this sort were proposed by Cowan,<sup>1</sup> Newal,<sup>2</sup> Bolton,<sup>3</sup> and notably Spurge<sup>4</sup> and Warnerke,<sup>5</sup> the last

<sup>1</sup> A. Cowan, *Brit. Journ.*, 1880, 430; *Brit. Journ.*, 1887, 194 and 210.

<sup>2</sup> Newal, *Brit. Journ.*, 1888, 584.

<sup>3</sup> Bolton, *Brit. Journ.*, 1889, 809.

<sup>4</sup> Spurge, *Phot. Journ.*, 1881, 44; *Brit. Journ.*, 1881, 675; *Phot. Journ.*, 1883, 159; *Journ. of Cam. Club*, 1893, 60.

<sup>5</sup> Warnerke, *Brit. Journ.*, 1881, 96 and 108.

named making several types of sensitometer which have been used to a very large extent.

This form of sensitometer has recently been revived by Mr. Chapman Jones<sup>1</sup> in his plate-tester.

In 1889 the Congrès International de Photographie de Paris<sup>2</sup> decided that the sensitiveness of a plate should be considered to be the exposure necessary to produce a definite density ( $\cdot 350$ )<sup>3</sup> upon the plate.

Since 1890 there have been developed two entirely different systems of sensitometry, the one in Germany and Austria and the other in England, and, curiously enough, they seem to be entirely confined to those countries.

The first method has logically developed from the old sensitometer method, and consists of an observation of the smallest amount of exposure necessary to give a visible image after development. This smallest exposure is termed the "Schwellenwerth" of the plate, and is determined by the aid of a rotating sector wheel and a constant light source. It has been developed by Scheiner,<sup>4</sup> and notably by Eder.<sup>5</sup> Originally there appears to have been an impression that this Schwellenwerth was a physical constant below which no action whatever occurred, but as it is quite easy to measure densities far below the Schwellenwerth by counting the number of silver grains under the microscope,<sup>6</sup> there is now no doubt that this value simply depends on the conditions and on the observer.

<sup>1</sup> Chapman Jones, *Phot. Journ.*, 1901, 246.

<sup>2</sup> A. Londe, *La Photographie Moderne*, Paris, 1896, 226.

<sup>3</sup> J. M. Eder, "System der Sensitometrie Photographischer Platten," 1 Abtheilung, *Sitzber. der K. K. Akad. der Wissenschaft*, Wien, 1889, sec. 2a.

<sup>4</sup> J. Scheiner, "Universal Sensitometer," *Eder's Jahrbuch*, 1895, 392 ; *Zeit. f. Inst. Kunde*, 1894, 201.

<sup>5</sup> J. M. Eder, *loc. cit.* ; also *Eder's Jahrbuch*, 1899, 37 ; *Ausführliche Handbuch d. Phot.*, 3<sup>te</sup> II ; Eder and Valenta, *Beiträge*, and translation in French, *Système de Sensitometrie*, by Belin.

<sup>6</sup> R. Abegg and Cl. Immerwahr, *Monatsschrift für Chemie*, 1900, 22, 88-94 ; *Arch. f. Wiss. Phot.*, 1900-1, II. 271 ; *Chem. Centralblatt*, 1901, II. 720.

In the following criticism of Dr. Eder's method of sensitometry, the references are to the French translation by M. Ed. Belin, published by Gauthier-Villars, Paris, as this is more likely to be accessible to English readers than the original papers, which are, however, reprinted in the *Photographische Correspondenz* in an accessible form. In the first place, it may be pointed out that it is always assumed that the sectors of the Scheiner wheel are perfectly cut ; Dr. Eder gives no calibration, and assumes that the errors are of so negligible a character that in constructing density curves it is utterly immaterial which set of gradations on the wheel is utilised, the exposure being adjusted to correspond. This assumption appears to us to require proof, as we have found sector wheels by no means easy to cut accurately.

On p. 13 the error of observation is stated to be  $1^{\circ}$  or  $2^{\circ}$  Scheiner at most—that is, 27 to 54 per cent. On pp. 50 and 51 the variation of the Scheiner number with the temperature of development is shown to be very great ; while on p. 54 the addition of potassium bromide to the developer is recommended, a proceeding which would greatly lower the Scheiner number, and lower it to different extents with different plates.

In 1890 there was published by Messrs. Ferdinand Hurter and Vero C. Driffield, in the *Journal of the Society of Chemical Industry*, a paper entitled "Photo-chemical Investigations," in the course of which they gave for the first time a method of determining the sensitiveness of plates which depends on the measurement of a series of densities instead of a single reading.

This method has been nominally adopted in England by most of the photographic plate-makers, but there has been some considerable doubt thrown on the fundamental experiments upon which it is founded, in view of which we decided to largely repeat those experiments, amplifying them, and, wherever possible, making them more accurate.

Messrs. Hurter and Driffield gave the following terminology, which has been generally adopted :—

$$T = \text{transparency} = \frac{I}{I'} = \frac{\text{intensity transmitted}}{\text{intensity incident}}$$

$$O = \text{opacity} = \frac{I'}{I}$$

$$D = \text{density} = \log_e O = -\log_e T \quad \text{in theoretical work}$$

$$= \log_{10} O = -\log_{10} T \quad \text{in practical photometry}$$

Messrs. Hurter and Driffield proved that the density was proportional to the mass of silver per square centimetre of the plate. This has been confirmed by Dr. Eder and also for a great number of experiments by the authors.<sup>1</sup>

The density was measured in a photometer, and the density — log exposure curve was plotted. The curve was of a *j* shape, and the central portion is approximately a straight line. If this straight portion is produced to cut the abscissa, the point at which it cuts is termed the inertia of the plate, while the speed is defined as inversely proportional to the inertia. Further, the slope of this straight line is found to vary with the development, and is termed the development factor.

Dealing only with this straight line, Messrs. Hurter and Driffield gave its equation in the form :—

$$D = \gamma(\log E - \log i)$$

where  $\gamma = \tan \theta = \text{slope}$ .

Further, they stated that this value *i*, the inertia, was a constant unaltered either by the time of development or the temperature or concentration of the developer (except with concentrated pyro developers), though they considered that it might be affected by the nature of the reducer or by the addition of potassium bromide.

Messrs. Hurter and Driffield also proved theoretically on certain assumptions, which appear to be reasonable, that this curve should conform to the general equation—

$$dx = \frac{I}{e} (1 - a)(e^{-kx} - e^{-ka})dt$$

<sup>1</sup> See Part I. p. 42.

which on integration, writing  $i = \frac{e}{k(1-a)}$ , gives—

$$D = \gamma \log_e \left\{ p - (p-1)\beta \frac{It}{i} \right\}$$

where  $p$  = opacity of the unexposed plate to blue light,

$$\log_e \beta = -\frac{1}{p},$$

and  $It = E$ , the exposure.

The value of  $i$  will clearly be expressed in the same units as those of  $E$ .

## ON THE EFFECT OF DEVELOPMENT ON THE INERTIA

### (1) Variation of the Time of Development.<sup>1</sup>

There is no difficulty in giving numerous examples of the constancy of the inertia with different times of development.

The following example will serve :—

TABLE 155.

Plate :—Barnet Photomechanical.

Plate A developed 4 mins.

Plate B developed 8 mins.

Log E.	D <sub>A</sub> .	D <sub>B</sub> .
2·60	2·96	—
2·26	2·69	—
2·10	2·47	—
1·92	2·192	3·16
1·59	1·692	2·40
1·213	1·044	1·47
0·863	0·612	0·884
0·516	0·304	0·496
0·140	0·102	0·228

Fig. 51. It will be seen that the inertias coincide.

This is found with all plates with but two exceptions—

(i.) In some plates the inertia steadily decreases with longer development, sometimes by large amounts. This is due to free potassium bromide in the plate, which acts in the same way as if it were in the developer (see later).

<sup>1</sup> See also Part II. p. 62.



(ii.) Occasionally plate curves are found which cross in the opposite sense to a slight degree. These are quite rare, but appear to occur beyond doubt. The variation of the inertia is usually small, and may be influenced mainly by fog.

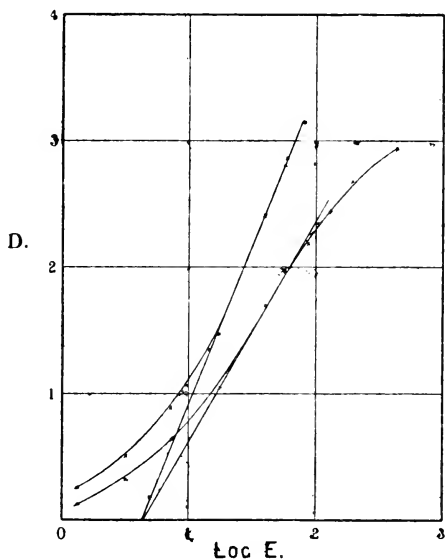


FIG. 51.

## (2) Variation of the Temperature of Development.

The following results will show that plates are not affected as to their inertias by the temperature of developer<sup>1</sup>:—

Plates were developed in the thermostat after it had been adjusted to various temperatures.

### Plate A.

Temperature C°	9·6°	20·8°
Log <i>i</i>	0·65	0·63

### Plate B.

Temperature C°	7·0°	16·3°
Log <i>i</i>	0·19	0·20

<sup>1</sup> Except with developers of very low reducing energy : *vide* p. 173.

The only effect of the change of the developing temperature is to change the velocity-constant of development.

### (3) Variation of the Concentration of the Developer.

#### (a) *Ferrous Oxalate.*

Messrs. Hurter and Driffield<sup>1</sup> state that half-saturated ferrous oxalate developer develops as great density as a saturated one.

We have found that with ferrous oxalate the time of development is rigidly inversely as the concentration for the same amount of density.<sup>2</sup>

#### (b) *Pyro Soda.*

Messrs. Hurter and Driffield (*loc. cit.*, p. 290 ff.) showed that considerable increases in the amount of pyrogallol in a pyro-soda developer produce lessened inertia.

We have confirmed this, thus, for a Gem colour plate—

$$\begin{array}{ll} \text{developed A } \frac{M}{100} \text{ pyrogallol} \\ \text{,, B } \frac{10}{M} \text{ pyrogallol} \end{array}$$

We obtained—

$$\log i_A = 0.45$$

$$\log i_B = 0.59$$

showing that strong pyrogallol solution acts as a restrainer.

This is probably true to some, though a lesser effect, with other organic developers.

### (4) Variation of the Reducing Agent.

This appears to be a very confused subject, a great number of diverse opinions being current. Messrs. Hurter and Driffield stated that the inertia was affected by the reducing agent employed.<sup>3</sup> It has even been stated that warm concentrated

<sup>1</sup> *Phot. Journ.*, 1898, 278, Exp. 5.

<sup>2</sup> See Part II. p. 64.

<sup>3</sup> *Brit. Journ.*, 39, 613, "A Standard Developer," Dr. Hurter and V. C. Driffield.

metol solution might divide the ferrous oxalate inertia by 51. We therefore considered it important to investigate this question carefully.

The result of this investigation seems to show that there are two important groups of plates in existence.

One group gives nearly the same inertia whatever reducer is employed.<sup>1</sup>

The other gives 1·75, the inertia with ferrous oxalate that it gives with organic developers.

Thus for the Wratten Ordinary—

	A (Ferrous oxalate).	B (Hydrokinone).
Log <i>i</i>	0·69	0·69

also—

	A (Fe Ox.).	B (Pyro).	C (Metol).	D (Rodinal).
Log <i>i</i>	0·75	0·76	0·73	0·73

Also a Seed plate gave—

	A (Ferrous oxalate).	B (Pyro).
Log <i>i</i>	1·34	1·36

And a Gem Process—

	A (Ferrous oxalate).	B (Pyro).
Log <i>i</i>	0·49	0·48

On the other hand, a Barnet Orthochromatic gave—

	A (Fe Ox.).	B (Pyro).	C (Hydrok.).	D (Rodinal).
Log <i>i</i>	1·698	1·44	1·40	1·41
Inertia	0·499	0·282		
Ratio	1·76	1		

Similarly, the Gem colour gave—

	A (Ferrous oxalate).	B (Pyro).
Log <i>i</i>	0·73	0·49
<i>i</i>	5·38	3·1
Ratio	1·74	1

And the Tricol—

	A (Ferrous oxalate).	B (Pyro).
Log <i>i</i>	0·67	0·45
<i>i</i>	4·69	2·82
Ratio	1·66	1

<sup>1</sup> The *energy* of the developer has some influence. See Part II. p. 196.

Wratten speed—

	A (Ferrous oxalate).	B (Pyro).
Log $i$ . . . .	1.53 . . . .	1.29
$i$ . . . . .	0.339 . . . .	0.195
Ratio . . . .	1.74 . . . .	1

There are a few plates which appear to be intermediate between these groups.

Thus a Wratten Allochrome<sup>1</sup> gave—

	A (Ferrous oxalate).	B (Pyro).
Log $i$ . . . .	1.91 . . . .	1.79
$i$ . . . . .	0.812 . . . .	0.589
Ratio . . . .	1.39 . . . .	1

It may be of service at this point to append a note upon fog in development. One of the most obvious defects introduced by developing in a thermostat is the somewhat increased fog produced, and we have therefore investigated the cause of this fog. Providing that the developing tubes and brass pots are perfectly clean, the plates developed in the thermostat have exactly the same amount of fog as those developed in a dish, but the washing in water before developing appears to always induce fog in fast plates.

The reason of this is not known to us, but it appears to be a fact, and hence, while plates must be washed when investigating development problems in order to ensure even diffusion, it may be better to omit the washing in practical sensitometry.

#### (5) On the Effect of Potassium Bromide upon the Inertia.

On the whole, our conclusions confirm those of Hurter and Driffeld in their 1898 paper, viz. that over the straight line portion of the curve an equal depression of density is produced. The theory as to this phenomenon is discussed in Part II. Chap. III. p. 92, and there a developed example is given of the influence on the inertia. From the sensitometrical standpoint the following experiments are of interest :—

<sup>1</sup> Original issue, 1904.

WRATTEN ORDINARY PLATE DEVELOPED FOR THREE MINUTES.

 A in  $\frac{N}{10}$  ferrous oxalate

 B in  $\frac{N}{10}$  ferrous oxalate,  $\frac{N}{100}$  KBr

TABLE 156.

Log E.	D <sub>A</sub> .	D <sub>B</sub> .	D <sub>A</sub> - D <sub>B</sub> .	
2'18	1'55	1'044	0'506	} Mean 0'493
1'89	1'34	0'862	0'478	
1'59	1'13	0'640	0'490	
1'30	0'902	0'414	0'488	
1'01	0'715	0'220	0'495	
0'75	0'532	0'100	0'432	

The regression of the inertia (as the phenomenon may be conveniently termed) with time of development is shown by the following results of the same plate developed in  $\frac{N}{10}$  ferrous oxalate,  $\frac{N}{100}$  KBr. C 4 mins., D 10 mins., and E 60 mins.

TABLE 157.

Log E.	D <sub>C</sub> .	D <sub>D</sub> .	D <sub>E</sub> .
2'182	1'724	2'832	—
1'890	1'470	2'622	4'10
1'591	1'242	2'270	3'39
1'297	0'958	1'824	2'77
1'009	0'646	1'394	2'08
0'750	0'360	0'916	1'474
0'508	—	0'586	1'034
0'141	—	0'220	0'388

If, however, these experiments are extended into the under- and over-exposed portions of the curve, it is found that the equal depression of the densities is a purely accidental phenomenon due to the measurements being made in the straight portion of the curve, the true law being that the whole curve is shifted sideways parallel to the exposure axis,

ON THE MATHEMATICAL RELATIONS OF THE FUNDAMENTAL  
EQUATION FOR A PLATE CURVE

If sufficiently accurate methods of coating, exposing, and measuring a plate be adopted, it will be found that the curve of density against logarithmic exposure obtained departs somewhat from a straight line even in the centre, and has a noticeable point of inflection. It will, moreover, be found that this curve is fitted very well by the theoretical equation given by Messrs. Hurter and Driffield, viz.—

$$D = \gamma \left\{ \log p - (p - 1) \beta^{\frac{E}{i}} \right\}$$

where  $p$  = the optical opacity of the unexposed plate to blue light,<sup>1</sup>

$$\log_e \beta = -\frac{1}{p},$$

$i$  = a constant,

$E$  = exposure,

$\gamma$  = a development constant.

Professor A. W. Porter, B.Sc. of University College, London, kindly assisted us in working out the inflection point of this equation.

If  $\gamma = 1$  the equation becomes—

$$D = \log_e \left\{ p - (p - 1) e^{-\frac{E}{pi}} \right\}$$

$$\text{whence } e^{\frac{E}{pi}} = \frac{p - 1}{p - e^D}$$

$$\text{Now, } \frac{dD}{dE} = \frac{p - e^D}{pie^D} \text{ and } \frac{dD}{d \log E} = \frac{(p - e^D)E}{pie^D}$$

$$\begin{aligned} \therefore \frac{d^2D}{dE \cdot d \log E} &= \frac{p - e^D}{pie^D} + \frac{E}{pi} \left( -\frac{p}{e^D} \right) \frac{p - e^D}{pie^D} \\ &= \frac{p - e^D}{pie^D} \left( 1 - \frac{E}{ic^D} \right) \end{aligned}$$

which is zero when  $e^D = \frac{E}{i}$ , which gives the point of inflection.

<sup>1</sup> But  $p$  must be taken in arbitrary units of about 10 times the real value. See H. J. Channon, *Phot. Journ.*, June, 1906, and discussion. The theoretical basis of the equation is probably wrong.

From this at the point of inflection—

$$D = \log_e \frac{E}{i}$$

and the slope is then—

$$\frac{p - \frac{E}{i}}{p}$$

If at the point of inflection  $\frac{E}{ip}$  is negligible compared with unity, the slope is equal to  $\gamma$ .

Expanding  $e^{\frac{E}{pi}}$ , and retaining only the first power of  $\frac{E}{pi}$ , we get—

$$1 + \frac{E}{pi} = \frac{p - 1}{p - \frac{E}{i}}$$

$$\text{whence } e^{\frac{E}{pi}} = \frac{E}{i} = \sqrt{p}$$

which gives the inflection point.

The straight line, which is tangential at this point, has the equation—

$$y - \log \sqrt{p} = \frac{p - \sqrt{p}}{p} (x - \log i \sqrt{p})$$

where  $x$  is the point where it cuts the abscissa when  $y = 0$ .

$$x = \log i - \frac{1}{2} \frac{\sqrt{p}}{p - \sqrt{p}} \log p$$

When calculating a plate curve, it is necessary to find  $i$  from this equation.

We may from this fundamental equation find the relation between the latitude of a plate and the opacity.

The latitude may be defined as the ratio of the exposure at which over-exposure commences to that at which under-exposure commences, and these two points must be arbitrarily defined.

From a series of guesses made in experimental work, we find that under-exposure becomes manifest when the slope of the line is equal to two-thirds of the development factor. On the other hand, over-exposure is noticeable when the slope

is one-half rather than two-thirds, the divergence in the curve not being so easily detected

In order to estimate the latitude, therefore, we must find the exposures at which the slope ( $\gamma$  being = 1) becomes  $\frac{1}{k}$ , where  $k$  can be of any amount.

Now the slope when  $\gamma = 1$ —

$$\begin{aligned} &= \frac{dD}{d \log E} = \frac{(p - e^v)E}{pie^v} \\ &= \frac{(p - 1)E}{pi \left\{ p \left( e^{\frac{E}{pi}} - 1 \right) + 1 \right\}} = \frac{1}{k} \text{ (say)} \end{aligned}$$

$$\begin{aligned} \text{whence } k(p - 1)E &= pi \left\{ p \left( e^{\frac{E}{pi}} - 1 \right) + 1 \right\} \\ &= p^2 i e^{\frac{E}{pi}} - pi(p - 1) \end{aligned}$$

$$\therefore \frac{E}{pi} + 2 \log p + \log i = \log (p - 1) + \log (kE + pi)$$

$$\therefore \frac{E}{pi} - \log (kE + pi) = \log (p - 1) - 2 \log p - \log i$$

or, writing  $C$  for  $pi$ —

$$\frac{E}{C} - \log (kE + C) = -A$$

This equation may be solved by trial and error for any value of  $k$  without great difficulty, but sufficiently accurate approximations can be obtained as follows:—

(1) For the under-exposure point. Since  $\frac{E^2}{p^2 i^2}$  is here of the order of  $\frac{1}{1000}$ , it is allowable to neglect all powers of  $\frac{E}{pi}$  beyond the first.

Whence expanding  $e^{\frac{E}{pi}}$ —

$$\begin{aligned} k(p - 1)E &= p^2 i \left( 1 + \frac{E}{pi} \right) - pi(p - 1) \\ \frac{k(p - 1)}{pi} E &= p \left( 1 + \frac{E}{pi} \right) - (p - 1) \\ &= p + \frac{E}{i} - p + 1 \end{aligned}$$



$$\frac{E}{i} \left( 1 - \frac{k(p-1)}{p} \right) = -1$$

or, since  $\frac{p-1}{p}$  is approximately equal to 1—

$$E = \frac{i}{k-1}$$

(2) For the over-exposure point. Here an approximation may be made by assuming  $E = \lambda ip$ .

And writing the approximate equation—

$$\frac{E}{ip \left( e^{\frac{E}{ip}} - 1 \right)} = \frac{1}{k}$$

we get  $\frac{\lambda}{e^{\lambda} - 1} = \frac{1}{k}$

whence we can find  $\lambda$  for any value of  $k$ .

This may be experimentally justified. Consider the following plates :—

Plate.	$i$ .	$p$ .
1 . . .	3 . .	100
2 . . .	0.2 . .	60

Then for the over-exposure points when  $k = \frac{3}{2}$  we get by trial and error (accurate) and by the approximation—

Plate	E (acc.).	E (by approx.).
1 . . .	218 . . .	216
2 . . .	8.9 . . .	8.0

The under-exposure point when  $\frac{1}{k} = \frac{2}{3}$  will, from the expression  $E = \frac{i}{k-1}$ , be at the point where  $E = 2i$ .

While over-exposure when  $\frac{1}{k} = \frac{1}{2}$  gives  $\lambda = 1.25$ , and  $E = 1.25pi$ .

Therefore the latitude  $= \frac{1.25pi}{2i} = 0.625p$ , and is independent of  $i$ .

In order to measure the latitude it is therefore only necessary to measure the opacity of the unexposed plate to blue-violet light.

It is necessary to be very careful in making this measurement owing to the great difficulty of measuring the density of diffusing media. It may be done in differential photometers by simply covering both sources with a strongly diffusing medium, though even in this case care must be taken to see that the density is measured throughout the region of sensitiveness of the plate—a very difficult task.

One of the best ways of measuring the opacity is to expose another plate of known inertia underneath the plate in the exposure machine, and to measure its apparent inertia, calculating from that the actinic light absorbed by the plate to be measured.

#### ON THE EFFECT OF THE INERTIA UPON THE EXPOSURES NECESSARY TO PRODUCE PRINTABLE NEGATIVES.

If two plates are taken, one of which is a plate with an inertia about 1, while the other has an inertia of about 0·2—that is to say, of one is what is commonly termed a slow plate, while the other is a fast plate—and they are given identical exposures so that both plates are under-exposed, it will be found that the difference between the negatives produced will be by no means so great as might have been supposed in view of the different inertias of the plates. In the case of extreme under-exposure with subjects of but little contrast, such, for instance, as focal plane snapshots in the open air, it will frequently be found that a slow plate capable of considerable forcing in development will give the best result possible at that exposure.

The cause of this phenomenon appears to lie in the fact that in the under-exposed portion of the curve increase of the development factor compensates for exposure.

Thus a plate gave the following under-exposure portion of the curve:—

Log E.	D.
0·3 . . . . .	0·101 × 3·9 = 0·393
0·6 . . . . .	0·158 × 3·9 = 0·615
0·9 . . . . .	0·246 × 3·9 = 0·960
1·2 . . . . .	0·391
1·5 . . . . .	0·626
1·8 . . . . .	0·981

It will be seen that multiplying the first three densities by 3.9 is equivalent to multiplying the exposure by 8.

This curious fact is, of course, only true for the underexposed portion of the curve, so that subjects of wide contrast which will include large portions of the region of correct exposure cannot be treated in this manner.

It will be easily seen from this that for working at the shortest possible exposures it is of greater importance to have a plate with a very high limiting development factor than a plate of great speed. The authors have taken very successful focal plane snapshots of  $\frac{1}{300}$  second and upwards, at  $f/6$ , upon Ilford half-tone plates and similar plates of low speed.

It may further be noticed from this how very unsuccessful attempts to judge inertias from camera exposures are likely to prove.

#### ON THE DEVELOPMENT FACTOR.

Our work on the theory of development has shown that the development factor can be accurately calculated under certain conditions, and we have urged the sensitometric value of the constants controlling it.

It must be understood that the following method is valid only for developers whose Watkins factor is less than 15 (see Part II. p. 186).

The conditions as to the use of the tables must be rigidly adhered to, otherwise results of quite misleading value will be obtained.

The method is that given in Part II. Chap. I. p. 65.

It was there shown that if two plates were developed for times  $t_1$  and  $t_2$ , such that  $t_2 = 2t_1$  and factors  $\gamma_1$  and  $\gamma_2$  are obtained—

$$\text{then (1) } K = \frac{1}{t} \log_e \frac{\gamma_1}{\gamma_2 - \gamma_1}$$

$$\text{and (2) } \gamma_x = \frac{\gamma_1}{1 - e^{-kt_1}} = \frac{\gamma_2}{1 - e^{-kt_2}}$$

The tables have been drawn up to facilitate calculations with these equations. Table A gives the relation between  $K$  and  $\frac{\gamma_2}{\gamma_1}$ ; Table B that between  $x$  and  $1 - e^{-x}$ .

Thus if  $t_1 = 2$  minutes—

$$\gamma_1 = 0.47\gamma_2 = 0.63 \frac{\gamma_2}{\gamma_1} = 1.34$$

$k$  for  $t_1 = 5$  minutes  $= 0.215$  (from table).

Whence  $k$  for  $t_1 = 2$  minutes  $= \frac{5}{2} \times 0.215 = 0.538$ .

NOTE.—If  $\gamma_2$  is greater than  $1.8 \gamma_1$ , it is necessary to repeat the experiment, developing twice as long.

TABLE A.

$k$ .	$\frac{\gamma_2}{\gamma_1}$	$\Delta$ for $\Delta$ 0.001 in $k$ .	$k$ .	$\frac{\gamma_2}{\gamma_1}$	$\Delta$ for $\Delta$ 0.001 in $k$ .
0.005	1.977	0.0050	0.205	1.358	0.0018
0.010	1.952	0.0048	0.210	1.349	0.0016
0.015	1.928	0.0050	0.215	1.341	0.0018
0.020	1.903	0.0046	0.220	1.332	0.0016
0.025	1.880	0.0044	0.225	1.324	0.0016
0.030	1.858	0.0042	0.230	1.316	0.0016
0.035	1.837	0.0040	0.235	1.308	0.0014
0.040	1.817	0.0040	0.240	1.301	0.0014
0.045	1.797	0.0038	0.245	1.294	0.0016
0.050	1.778	0.0038	0.250	1.286	0.0016
0.055	1.759	0.0036	0.255	1.278	0.0014
0.060	1.741	0.0034	0.260	1.271	0.0014
0.065	1.724	0.0034	0.265	1.264	0.0014
0.070	1.717	0.0032	0.270	1.257	0.0012
0.075	1.691	0.0032	0.275	1.251	0.0012
0.080	1.675	0.0030	0.280	1.245	0.0012
0.085	1.660	0.0032	0.285	1.239	0.0012
0.090	1.644	0.0032	0.290	1.233	0.0012
0.095	1.628	0.0032	0.295	1.227	0.0012
0.100	1.612	0.0032	0.300	1.221	0.0010
0.105	1.596	0.0032	0.305	1.216	0.0012
0.110	1.580	0.0030	0.310	1.210	0.0010
0.115	1.565	0.0028	0.315	1.205	0.0010
0.120	1.551	0.0028	0.320	1.200	0.0010
0.125	1.537	0.0028	0.325	1.195	0.0008
0.130	1.523	0.0026	0.330	1.191	0.0010
0.135	1.510	0.0028	0.335	1.186	0.0008
0.140	1.496	0.0024	0.340	1.182	0.0008
0.145	1.484	0.0024	0.345	1.178	0.0008
0.150	1.472	0.0024	0.350	1.174	0.0010
0.155	1.460	0.0024	0.355	1.169	0.0008
0.160	1.448	0.0022	0.360	1.165	0.0008
0.165	1.437	0.0022	0.365	1.161	0.0008
0.170	1.426	0.0022	0.370	1.157	0.0006
0.175	1.415	0.0020	0.375	1.154	0.0008
0.180	1.405	0.0018	0.380	1.150	0.0006
0.185	1.396	0.0018	0.385	1.147	0.0008
0.190	1.387	0.0020	0.390	1.143	0.0008
0.195	1.377	0.0018	0.395	1.139	0.0006
0.200	1.368	0.0020	0.400	1.136	

TABLE B (for equation 2).

To use this table find against the value of  $kt$  the corresponding value of  $1 - e^{-kt}$  and divide the  $\gamma$  by this to get  $\gamma_x$ .

Thus if  $k = 0.538$ .

$$kt_1 = 1.076. \quad 1 - e^{-kt_1} = 0.6612$$

$$\gamma_x = \frac{0.47}{0.6612} = 0.710$$

$kt$ .	$1 - e^{-kt}$ .	$\Delta$ for 0.01 in $kt$ .	$kt$ .	$1 - e^{-kt}$ .	$\Delta$ for 0.01 in $kt$ .
0.000	0.0000	0.0095	1.000	0.6322	0.0034
0.025	0.02		1.025	0.6485	
0.050	0.046		1.050	0.6547	
0.075	0.073		1.075	0.6609	
0.100	0.0952		1.100	0.6671	
0.125	0.1174	0.0086	1.125	0.6741	0.0032
0.150	0.1387		1.150	0.6830	
0.175	0.1600		1.175	0.6909	
0.200	0.1813		1.200	0.6988	
0.225	0.2082		1.225	0.7059	
0.250	0.2252	0.0077	1.250	0.7131	0.0029
0.275	0.2422		1.275	0.7203	
0.300	0.2592		1.300	0.7275	
0.325	0.2769		1.325	0.7339	
0.350	0.2945		1.350	0.7403	
0.375	0.3121	0.0071	1.375	0.7469	0.0026
0.400	0.3297		1.400	0.7534	
0.425	0.3458		1.425	0.7592	
0.450	0.3617		1.450	0.7651	
0.475	0.3776		1.475	0.7710	
0.500	0.3935	0.0064	1.500	0.7769	0.0024
0.525	0.4085		1.525	0.7822	
0.550	0.4234		1.550	0.7875	
0.575	0.4373		1.575	0.7928	
0.600	0.4512		1.600	0.7981	
0.625	0.4641	0.0057	1.625	0.8029	0.0022
0.650	0.4772		1.650	0.8077	
0.675	0.4903		1.675	0.8125	
0.700	0.5034		1.700	0.8173	
0.725	0.5158		1.725	0.8215	
0.750	0.5281	0.0052	1.750	0.8259	0.0017
0.775	0.5394		1.775	0.8303	
0.800	0.5507		1.800	0.8347	
0.825	0.5613		1.825	0.8387	
0.850	0.5714		1.850	0.8426	
0.875	0.5827	0.0047	1.875	0.8465	0.0016
0.900	0.5934		1.900	0.8504	
0.925	0.6031		1.925	0.8539	
0.950	0.6128		1.950	0.8575	
0.975	0.6225		1.975	0.8611	

$kt.$	$1 - e^{-kt}$	$\Delta$ for 0.01 in $kt.$	$kt.$	$1 - e^{-kt}$	$\Delta$ for 0.01 in $kt.$
2.000	0.8647	0.0013	3.000	0.9502	0.00047
2.025	0.8680		3.025	0.9513	
2.050	0.8712		3.050	0.9525	
2.075	0.8744		3.075	0.9537	
2.100	0.8776	0.0012	3.100	0.9549	0.00043
2.125	0.8805		3.125	0.9559	
2.150	0.8834		3.150	0.9570	
2.175	0.8863		3.175	0.9581	
2.200	0.8892	0.00105	3.200	0.9592	0.00039
2.225	0.8919		3.225	0.9601	
2.250	0.8945		3.250	0.9611	
2.275	0.8971		3.275	0.9621	
2.300	0.8997	0.00096	3.300	0.9631	0.00036
2.325	0.9021		3.325	0.9639	
2.350	0.9045		3.350	0.9648	
2.375	0.9069		3.375	0.9657	
2.400	0.9093	0.00086	3.400	0.9666	0.00032
2.425	0.9113		3.425	0.9674	
2.450	0.9135		3.450	0.9682	
2.475	0.9157		3.475	0.9690	
2.500	0.9179	0.00078	3.500	0.9698	0.00029
2.525	0.9197		3.525	0.9706	
2.550	0.9217		3.550	0.9713	
2.575	0.9237		3.575	0.9720	
2.600	0.9257	0.00071	3.600	0.9727	0.00026
2.625	0.9274		3.625	0.9732	
2.650	0.9292		3.650	0.9739	
2.675	0.9310		3.675	0.9746	
2.700	0.9328	0.00064	3.700	0.9753	0.00023
2.725	0.9344		3.725	0.9758	
2.750	0.9360		3.750	0.9764	
2.775	0.9376		3.775	0.9770	
2.800	0.9392	0.00058	3.800	0.9776	0.00022
2.825	0.9408		3.825	0.9780	
2.850	0.9412		3.850	0.9786	
2.875	0.9426		3.875	0.9792	
2.900	0.9450	0.00052	3.900	0.9798	0.00019
2.925	0.9463		3.925	0.9802	
2.950	0.9476		3.950	0.9807	
2.975	0.9489		3.975	0.9812	
			4.000	0.9817	

For a Bibliography of this subject, see *Phot. Journ.*, Nov., 1904.

## CHAPTER II

### THE EFFECT OF THE WAVE-LENGTH OF THE INCIDENT LIGHT UPON THE GRADATION PRODUCED

**Bibliography.**—*Phot. Journ.*, June, 1900, p. 279, "The Effect of Wave-length upon Gradation." Chapman Jones.

*Phot. Journ.*, June, 1900, p. 286, "Hydroquinone and Colour Impressions." Alfred Watkins. With discussion.

*Proc. of Roy. Soc.*, No. 68, 1901, p. 300, "On the Variation in Gradation of a Developed Photographic Image when impressed by Monochromatic Light of Different Wave-lengths." W. de W. Abney.

*Zeit. für Wiss. Phot.*, II., H. 12, S. 419, "Notiz über die spektrale Veränderlichkeit der Gradation von Bromsilbergelatineplatten." Ejnar Hertzsprung.

*Journ. of the Camera Club*, vol. 13, 1899, p. 173. Eder's Jahrbuch, 1900, 302, "Effect of Thickness of the Film on the Image, and on the Sensitiveness of the Plate." Sir W. de W. Abney.

**History.**—Mr. Chapman Jones gives the results of his paper in the following summary :—

(1) Gradation is not constant with varying wave-length.

(2) The longer the wave-length, the steeper the gradation, except that it becomes less steep in the higher densities (the tendency to reversal being greater, the longer the wave-length), and also probably less steep in the lowest densities. The tendency apparently is to change in the opacity logarithm (or "density") curve in the direction shown by a curve given (I give later several curves showing this tendency).

(3) The differences in gradation are not due to different compounds in the film when specially sensitised, because they

are shown in ordinary plates, and an increase in the difference of wave-length gives an increase in the difference of gradation irrespective of the sensitising of the plate.

(4) The use of pyrogallol and ammonia leads to irregularity in this matter, as in others, making the curve produced by the light of longer wave-length less steep than it otherwise would be (or that of a shorter wave-length more steep). It seems probable that it is the ammonia that leads to the irregularity.

Sir W. de W. Abney finds results almost identical with those published by Mr. Chapman Jones, with this difference, that Abney finds "that the gradation is least steep at the region of maximum photographic effect and increases in steepness on both sides of the region."

In neither of these investigations were precautions taken to keep the photographic intensity of the light source constant with different colours, and this would, as Sir W. Abney points out,<sup>1</sup> produce different "steepness of gradation" itself.

**Discussion of these Results.**—In considering the results attained, the great difficulty which arises is connected with the meaning to be assigned to the word "gradation."

The effect of light action upon a plate is represented with fair accuracy by the equation<sup>2</sup>—

$$D = \gamma \log \left\{ p - (p - 1)\beta^{\frac{E}{i}} \right\}$$

where  $\log_e \beta = -\frac{1}{p}$ , and  $p$  = optical opacity of the unexposed plate, and  $\gamma$  = a development factor.  $D$  = mass of silver made reducible.

Now, gradation may mean either  $\gamma$  or it may mean the differential coefficient  $\frac{dD}{d \log E}$ , when  $\gamma = 1$ .

The word is often used in both senses, and sometimes means  $\gamma$ , sometimes  $\frac{dD}{d \log E}$ , and sometimes  $\frac{\gamma dD}{d \log E}$ .

<sup>1</sup> *Loc. cit.*, p. 297.

<sup>2</sup> Hurter and Driffield, *Photo-chem. Investigation*, *J. S. C. I.*, May, 1890.

[NOTE.—It is immaterial whether Hurter and Driffield's equation is correct or not; the main conclusions as regards the *slopes* remain the same.]



In a mathematical discussion on the plate-curve<sup>1</sup> we obtained certain results which are of importance upon this question.

These results are—

$$(1) \quad \frac{dD}{d \log E} = \frac{(p - e^D)E}{pie^D}$$

From this it follows that if  $p$  is large,  $\frac{dD}{d \log E}$  is nearly 1 for a large portion of the curve, and  $\gamma$  can be deduced simply by drawing a straight line through these points (the method pursued by Messrs. Hurter and Driffield).

If  $p$  is small the "straight" portion becomes very small, and it is necessary to deduce  $\gamma$  from the tangent to the inflection point to which it is related by the equations.

(2) At the inflection point—

$$D = \log_e \frac{E}{i}$$

$$\text{and (3) } \gamma = \frac{p}{p - \frac{E}{i}} \text{ slope of tangent}$$

where  $E$  = exposure for inflection point.

As has already been stated,  $\gamma$  is a factor fixed by development, and it has been further shown<sup>2</sup> that the equation connecting  $\gamma$  with the time of development is—

$$\gamma = \gamma_{\infty}(1 - e^{-\kappa t})$$

where  $\gamma_{\infty}$  is the ultimate development factor attainable with infinite development, and is dependent on the plate; while  $\kappa$  is the "velocity constant" of development, and depends partly on the plate and partly on the temperature, concentration, etc., of the developer.

The investigation here detailed was, therefore, undertaken with a view to finding whether—

$$(1) \quad \frac{dD}{d \log E}, \quad \text{or (2) } \gamma, \quad \text{or (3) } \frac{\gamma dD}{d \log E}$$

<sup>1</sup> *Phot. Journ.*, November, 1904, p. 294; also p. 259.

<sup>2</sup> *Ibid.*, February and July, 1903; also p. 65.

were the factors altered by the wave-length of the incident light.

It is of especial interest to find whether  $\gamma$  can be affected by the incident light, because this would imply that either  $\kappa$  or  $\gamma_{\infty}$  were altered. The first alternative is almost inconceivable, since it would imply various kinds of chemical or physical alterations in the silver bromide with differently coloured incident light.

The second alternative, various  $\gamma_{\infty}$ 's, is not so easily disposed of, and, if such an effect occurred, would probably prove of very great importance.

Hertzprung<sup>1</sup> has attempted to trace a connection between the optical opacity ( $p$ ) and gradation on certain assumptions of his own. These assumptions appear, however, to lead to a formula which does not truly represent the plate-curve, and the attempt largely fails, Hertzprung stating that the optical opacity is only one of the factors operating.

**Experimental Methods.**—These experiments were conducted in the authors' exposure instrument,<sup>2</sup> the colour of the light being adjusted by fluid filters.

Various burners were used, notably a large water-cooled acetylene burner.

Inasmuch as the qualitative phenomena to be observed were well known, it was sufficient to simply obtain quantitative measurements of two extreme points.

The following two filters were therefore used :—

*For the violet*—methyl violet in one cell, 1 cm. thick ; ammonio-copper sulphate, 2 per cent., in another cell ; adjusted till band 4825–4510 was passed ; and darkened with dilute chromic acid in a third cell until the photographic intensity for each plate used was nearly that of the red screen.

*For the red*—2N chromic acid in one cell, 1 cm. thick ; red glass ; band passed 5900 to end of spectrum.

The optical opacities of the unexposed plates were measured in the spectrophotometer with milk-glass to avoid scatter error.

<sup>1</sup> *Loc. cit.*, p. 297.

<sup>2</sup> For description of all the instruments employed, see Introductory chapter, p. 10.

**Experimental Results.**—(a) *Ordinary Plates.*—The Barnet extra rapid plate was taken.

Opacity measured—

Red. . . W.L. 6500  $O = 3.28$   $\log = 0.516$

Violet . . W.L. 4600  $O = 15.75$   $\log = 1.196$

Taking  $i = 1$  and  $\gamma = 1$ , we may calculate the value of the expression—

$$D = \log_{10} \left\{ p - (p - 1)e^{-\frac{E}{p}} \right\}$$

for the two values of  $p$  (3.28 and 15.76).

*Results*—

TABLE 158.

E.	$e^{-\frac{E}{p_1}}$	$e^{-\frac{E}{p_2}}$	$D_1$ .	$D_2$ .	Log E.
0.5	0.835	0.968	0.124	0.178	1.7
1.0	0.7373	0.938	0.205	0.283	0
2.0	0.5436	0.883	0.310	0.439	0.3
4.0	0.2954	0.777	0.417	0.637	0.6
8.0	0.0871	0.6013	0.488	0.829	0.9
16.0	0.0076	0.3671	0.514	1.015	1.2
32.0	0.000057	0.1345	0.517	1.139	1.5
64.0	—	0.01818	—	1.190	1.8
128.0	—	0.00029	—	1.196	2.1

Fig. 52 shows these results.

Exposure of Barnet extra rapid plates through red and violet screens.

*Results*—

TABLE 159.

Log E.	$D_{\text{red.}}$	$D_{\text{violet.}}$
2.60	1.470	1.283
2.30	0.958	0.850
2.00	0.514	0.384
1.70	0.195	0.161
1.40	0.090	0.077

Exposure one hour to large water-cooled burner.

These figures give no satisfactory results, the exposure being too small to get into the over-exposed portion.

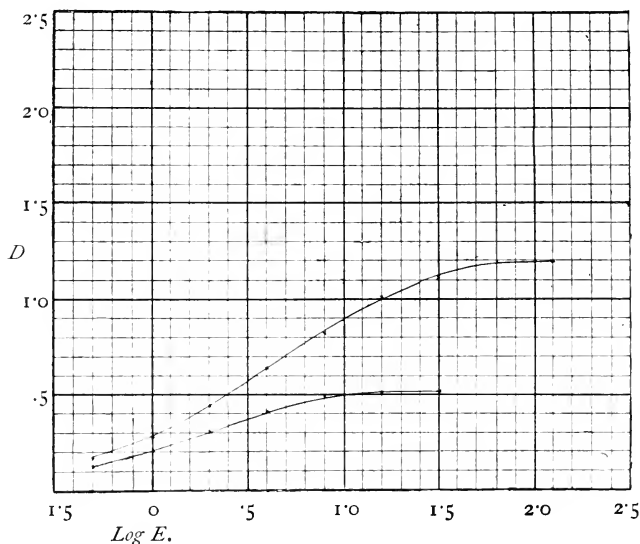


FIG. 52.

An exposure of 14 hours, however, showed that the red curve did bend in the way shown by Fig. 52.

TABLE 160.

Log E.	$D_{\text{red.}}$
3.75	1.260
3.45	1.240
3.15	1.18
2.85	0.944
2.55	0.713
2.25	0.377
1.95	0.090

(FIG. 53.)

If the last density in Fig. 52 on the straight portion be divided by the inertia, we get a value, of about 10 for the red

curve. This curve gives the same value, though comparisons are difficult. We can, however, by altering the  $\gamma$  of Fig. 52 (red), get a series of densities which we can interpolate on Fig. 53.

Thus multiplying the red curve by 2.44, we get 0.304, 0.500, 0.754, 1.02, 1.19, 1.255, 1.260 for the results which are shown as circular points on Fig. 53.

The result is not very satisfactory, but shows that the difference in the opacities is quite sufficient to account for the observed effect.

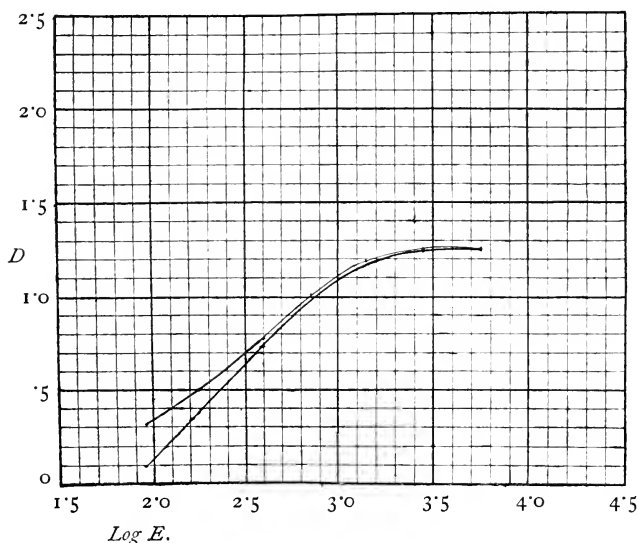


FIG. 53.

Naturally experiments with red light on ordinary plates are by no means easy to make, and it seemed desirable to make further experiments on orthochromatic plates.

(b) *Orthochromatic Plates*.—Gem tricol-sensitised process plate used. Plates exposed to red and violet and developed for 5 and 10 minutes.

*Results—*

TABLE 161.

Log E.	$D_{\text{red } 5.}$	$D_{\text{red } 10.}$	Log E.	$D_{\text{violet } 5.}$	$D_{\text{violet } 10.}$
2.60	1.860	2.59	3.10	1.934	2.23
2.30	1.59	2.12	2.80	1.424	1.734
2.00	1.14	1.364	2.50	0.838	1.089
1.70	0.592	0.664	2.20	0.355	0.404
1.40	0.221	0.244	1.90	0.112	0.136
1.10	0.036	0.074	—	—	—
$\gamma$ (from curves)	1.95	2.35	—	1.80	2.18

$\log i_{\text{red}} = 1.42$  ;  $\log i_{\text{violet}} = 1.50$ .

Violet log E's altered by adding 0.5 to keep curves from crossing.

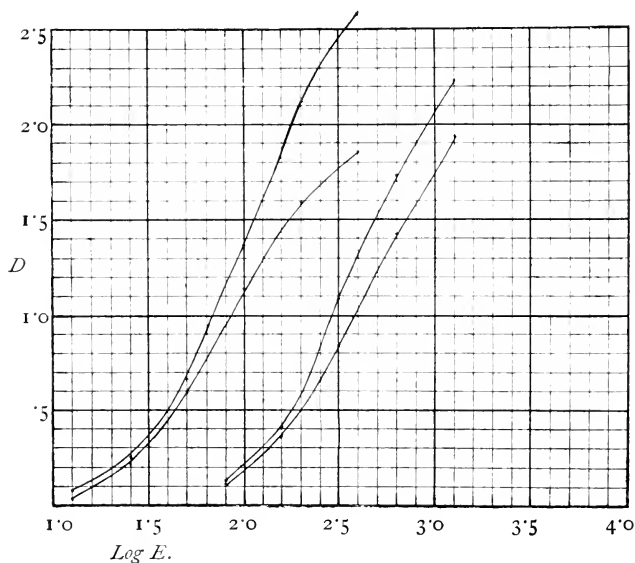


FIG. 54.

Notice the quicker bending of the red curve.

It will easily be seen that the  $\gamma$ 's do not differ greatly.

The experiment was repeated with hydroquinone developer.

Results for Gem tricol developed 5 and 10 minutes with  $\frac{M}{20}$  hydrokinone—

TABLE 162.

Log E.	D <sub>red 5.</sub>	D <sub>red 10.</sub>	D <sub>violet 5.</sub>	D <sub>violet 10.</sub>
2.60	1.934	2.56	scratched film	2.59
2.30	1.54	1.962	1.624	2.34
2.00	0.896	1.283	1.174	1.76
1.70	0.350	0.689	0.550	0.99
1.40	0.160	0.207	0.126	0.350
1.10	—	0.027	—	0.073
$\gamma$	1.86	2.23	1.82	2.27

Again, it is the shape of the curve, and not  $\gamma$ , which is altered.

$$\log i_{\text{red}} = 1.43; \log i_{\text{violet}} = 1.26$$

A point worth noting is that while  $\log i_{\text{red}}$  is constant,  $\log i_{\text{violet}}$  has dropped from 1.50 to 1.26 on substituting hydrokinone for ferrous oxalate. That is—

$$\frac{i_{\text{FeO}}}{i_{\text{hydro.}}} = 1.74$$

In another portion of this work<sup>1</sup> (*Phot. Journ.*, November, 1904, p. 287) it is shown that plates of this type to which the tricol belongs give—

$$\frac{i_{\text{FeO}}}{i_{\text{organic devel.}}} = 1.75$$

But that the tricol only gave 1.66.

This experiment shows the reason of this. It is only the violet inertia which is affected by the ferrous oxalate, the "orthochromatic inertia" being unaffected.

This unaffected portion in the tricol is about one-twelfth of the total sensitiveness.

To explain the results given in the *Phot. Journ.*, November, 1904, p. 287, experiments were made by soaking plates in

<sup>1</sup> Vide p. 285.

ammonia solution, fuming them, etc., and the conclusion was come to that the curve of the difference in  $\log i$ 's was a very slight amount of ammonia fuming, which depresses the ferrous oxalate inertia.

In order to make a final test as to the question of the alteration in gradation, some special Mawson Ortho B plates were obtained of a slow emulsion, and very excellently coated on patent plate by the kindness of Mr. J. B. Payne.

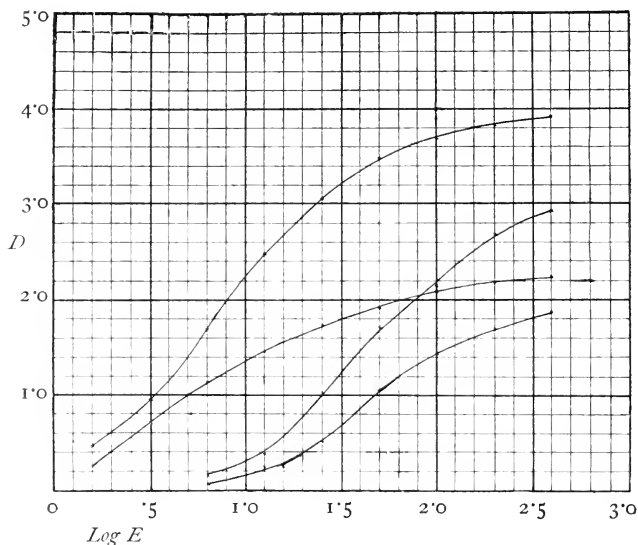


FIG. 55.

The constants for these plates were as follows :—

$$\begin{aligned}
 i &= 1.10 \\
 \gamma_{\infty} &= 2.50 \\
 K &= 0.121
 \end{aligned}
 \qquad
 \frac{\text{blue sens.}}{\text{yellow sens.}} = 8.91$$

These plates were then exposed behind the red and violet screens, and were developed for 10 and 20 minutes.



## Results—

TABLE 163.

Log E.	Red D <sub>10</sub> .	Red D <sub>20</sub> .	Violet D <sub>10</sub> .	Violet D <sub>20</sub> .
2'60	2'25	3'93	1'88	2'93
2'30	2'19	3'83	1'71	2'69
2'00	2'09	3'71	1'424	2'16
1'70	1'92	3'48	1'05	1'72
1'40	1'76	3'06	0'523	1'02
1'10	1'47	2'47	0'245	0'386
0'80	1'146	1'71	0'083	0'151
0'50	0'71	0'96	—	—
0'20	0'267	0'46	—	—
$\gamma$	1'34	2'20	1'36	2'15

These results confirm the conclusions arrived at, namely—

(1) Alteration of the wave-length of the incident light affects

$\frac{dD}{d \log E}$ , but not  $\gamma$ .

(2) The alteration of  $\frac{dD}{d \log E}$  can be accounted for by the differences in the value of  $p$ , which exist with differently coloured lighting.

NOTE.—Since this work was done, Precht and Stenger have published a considerable amount of work on the subject (*Zeit. wiss. Phot.*, **III.**), and the isocyanine dyes described in the next section have come into use, so that the work requires confirmation. But the main conclusions are probably accurate. This is confirmed by E. Lohmeier, who has measured the gradation of plates bathed in the isocyanines in Miethe's laboratory, Berlin.

## CHAPTER III

### THE ESTIMATION OF THE COLOUR-SENSITIVENESS OF PLATES

**Introduction.**—From the earliest days of photography, attempts have been made to measure, and usually to represent graphically, the distribution of the sensitiveness of a plate with regard to the spectrum. In the earlier measurements<sup>1</sup> a plate was exposed in the spectroscope and eye estimations of the density were made and plotted against the wave-length.

Later<sup>2</sup> this method was improved, a large number of plates of each brand being used; these were exposed one by one in a patch of monochromatic light of differing colours of the spectrum, and developed together.

On noting the sensitiveness to each colour, a curve may be constructed showing the sensitiveness for different wave-lengths. In 1888<sup>3</sup> Sir W. de W. Abney had again improved his method, and had practically reduced it to the final form possible. He now impressed on one plate both the spectrum and also a series of differing exposures to white light, and, after measurement of the opacities of the spectral exposure, interpolated these between those of the scaling exposure, thus obtaining a curve of equivalent intensities incident, which has the great

<sup>1</sup> W. de W. Abney, *Phot. Journ.*, May, 1882.

<sup>2</sup> Abney, Bakerian Lecture, *Proc. Roy. Soc.*, 1880; *Phot. Journ.*, 1881, p. 95; also "Notes on the Effect of the Spectrum on the Haloid Salts of Silver and on Mixtures of the Same," *Phot. Journ.*, 1882, p. 154.

<sup>3</sup> *Phot. Journ.*, November, 1888.

advantage that it is independent of the development of the plate and also to a considerable extent of the exposure which the plate has received. While some method of exposure to the spectrum is clearly necessary, it has the great disadvantage that the results obtained are almost incapable of brief expression, and must be presented in some graphic form. This fact has caused many attempts to be made to use not pure spectrum colours but mixtures of colour, and instruments of this type are usually termed colour sensitometers. In the discussion of these methods of measurement there is a tendency in the desire to obtain practical tests to forget that, after all, what is really wanted is a searching test which will accentuate differences as far as possible. If, for instance, pigment sensitometers are employed giving large amounts of reflected white light, it is perfectly true that these large amounts of reflected white light occur in all practical photography, but, at the same time, they are not what it is desired to measure. If it is desired to find the relative sensitiveness of a plate to blue and to yellow, then the effect of diluting both colours with white is simply to obscure the effect, and frequently to create a completely false impression.

The first of these integrating colour sensitometers was devised by Abney,<sup>1</sup> and consisted of a series of colour glasses, each letting through a band of spectral colour and all of the same luminosity.<sup>2</sup> A perfectly orthochromatic plate will therefore render all these patches of the same density. This sensitometer has been included by Mr. Chapman Jones in his plate tester. Of making colour charts to serve as sensitometers there is no end, by far the most practical and useful being the disc sensitometers of Sir W. de W. Abney. The chief objection to the Abney sensitometer is that it does not give a scale of tones but only one tone, and it appears distinctly better to divide up the spectrum into sections, and measure the sensitiveness of the plate to each section. If the sections are very small, we have our spectrum curve again; but if we have only two or three

<sup>1</sup> "Orthochromatics: Colour Sensitometry," *Phot. Journ.*, June, 1895

<sup>2</sup> Originally the luminosities were equalised by means of a rotating sector.

sections, it is possible to easily express the sensitiveness of the plate to these sections. Thus we see that the ideal towards which we may aim in colour sensitometry is to have a spectro-sensitometer with which we may expose plates either to a series of pure colours or to broad bands of colours. Hitherto this has not been realised; but inasmuch as it now seems to be practicable, it appeared desirable to publish the preliminary work which has already been accomplished, and to indicate the lines along which this work may be developed. The method which has been adopted by Dr. Eder for colour sensitometry consists of the use of integrating colour filters of the broadest type. In the earlier work the spectrum was divided into two just at the limit of sensitiveness of an ordinary plate (about W.L. 4950), and the ratio of the sensitiveness to these two portions of the spectrum measured.<sup>1</sup> Later<sup>2</sup> he divided the spectrum into three regions—blue-violet, green, and orange-red. E. J. Wall<sup>3</sup> also employs three screens, making his red screen of Tolan Red.

Thus it will be seen that this discussion must be divided into three parts: (a) The methods of obtaining the spectrum curve. (b) The methods of using broad-banded light filters. (c) The possibility of combining these two systems into a general system of spectro-sensitometry.

(a) The methods of obtaining the spectrum curve. This spectrum curve may have ordinates representing—

- Either (1) the density of the developed plate ;
- or (2) equivalent intensities of white light ;
- or (3) some sensitiveness number.

Of these, (3) is certainly the most desirable, but is also the most difficult of attainment, and hitherto the choice has lain between (1) and (2).

The chief objection to interpolating the measured density

<sup>1</sup> J. M. Eder, *System de Sensitometrie*, III.

<sup>2</sup> "Über die sensitometrische Prüfung gewöhnliche und orthochromatischer Platten," *Phot. Korr.*, 1903, p. 426.

<sup>3</sup> E. J. Wall, "The Testing of Orthochromatic Plates," *Phot.*, 1904, II. 368.

into the density-exposure curve, and so obtaining the equivalent intensity, is that this density-exposure curve is not fixed, but varies with the wave-length of the incident light,<sup>1</sup> so that the results are very far from accurate. Moreover, the uncertainty as to spectral distribution of intensity and energy distribution of light-source employed makes all spectral exposures merely qualitative and comparative, and for this purpose measurements of the density itself appear to be sufficient. In fact, the chief information to be obtained from a spectrum curve is as to shape (*i.e.* maxima and minima), the actual height of the curve in any part (which, of course, varies with the time of development) being an entirely secondary matter. For quantitative information as to the distribution of sensitiveness, it would appear to be better to trust to the measurements made behind broad-banded filters rather than attempt to make ordinary exposure to the spectrum more definite.

There are, however, two common sources of error in spectrum exposures which lead to misleading conclusions as to the shape of the curves. These are, (1) abnormality of dispersion; (2) unusual distribution of intensity in the light-source employed.

The first cause is, of course, particularly noticeable in the case of prismatic spectroscopes, and all such should be carefully avoided. The spectroscope used in this work was one of those little prism grating spectroscopic cameras for which we have to thank Mr. Tallent, and even in this the abnormality is considerable, the dispersion from 3500–4500 being 13·3 times that from 6000–7000.

The second cause of error is much more misleading because less understood and frequently unstated. A great part of the

<sup>1</sup> Chapman Jones, "The Effect of Wave-length upon Gradation," *Phot. Journ.*, June, 1900; W. de W. Abney, "On the Variation in Gradation of a Developed Photographic Image when impressed by Monochromatic Light of Different Wave-lengths," *Proc. Roy. Soc.*, **68**, 300.

Ejnar Hertzsprung, "Notiz über die spektrale Verändlichkeit der Gradation von Bromsilber gelatine platten," *Z. W. P.*, **II**, H. 12, S. 419. Also Chapter II. of this Part.

discussion which followed Messrs. Newton and Bull's paper on orthochromatic plates<sup>1</sup> was due to a misunderstanding of the effect of the light used.<sup>2</sup> For example, in that paper it was stated that bathing a plate in orthochrome T increased the speed 15 times. This is perfectly true for the light used (incandescent gas), but the speed measured by daylight is not appreciably affected by bathing.

The subject has, however, been discussed by many authors,<sup>3</sup> and the general conclusion reached has been that the light to be used for testing plates should be diffused daylight. Now, adopting the acetylene burner as a source, a filter has already been designed and described<sup>4</sup> which reduced the acetylene light to daylight to a sufficient extent to give the correct speed for orthochromatic plates compared with ordinary plates. This, however, was not nearly correct when tested throughout the whole of the spectral range, being deficient both in the extreme violet and in the red. It let through far too much red, while the failure of the acetylene flame to supply sufficient violet and ultra-violet was insufficiently compensated. The only way in which this last defect could be set right was to darken all the rest of the spectrum, but the red could be adjusted correctly by the use of an extra copper acetate filter.

The method of work adopted was to take photographs on panchromatic plates in the Tallent spectrocope, altering the screen in front of the burner until the screened acetylene gave exactly the same curve as daylight. Thus the following results were obtained at the commencement:—

<sup>1</sup> "A Comparison of Orthochromatic Plates," *Phot. Journ.*, October, 1903.

<sup>2</sup> Not a misunderstanding by the authors of that paper, of course.

<sup>3</sup> Abney, *Phot. Journ.*, 1882, p. 121; S. Davis, *Phot. Journ.*, 1884, p. 57 (Discussion); V. Schumann, *Phot. Rund.*, 21. 167; G. F. Williams, *B. J.*, 40. 229; J. M. Eder, *Phot. Korr.*, 1903, p. 426; A. Payne, *Phot.*, 1904, I. p. 471; E. J. Wall, *Phot.*, 1904, II. p. 368.

<sup>4</sup> Mees and Sheppard, *Phot. Journ.*, November, 1904, p. 292.

PLATE USED, WRATTEN ORDINARY, BATHED IN PINACYANOL.

Wave-length.	Density.	Density.	Density.
	Daylight.	Acetylene screened.	Screen and extra cu. acetate cell.
6800	0·692	1·520	0·291
6700	1·03	1·962	0·380
6600	1·16	1·948	0·488
6500	1·256	1·854	0·650
6400	1·330	1·630	0·846
6300	1·38	1·580	1·025
6200	1·42	1·58	1·108
6100	1·455	1·52	1·124
6000	1·490	1·43	1·174
5900	1·610	1·432	1·330
5800	1·670	1·496	1·550
5700	1·670	1·58	1·59
5600	1·616	1·616	1·59
5500	1·58	1·58	1·528
5400	1·58	1·607	1·496
5300	1·63	1·600	1·438
5200	1·607	1·432	1·401
5100	1·538	1·58	1·222
5000	1·330	1·57	1·078
4900	1·309	1·594	1·027
4800	1·512	1·394	1·350
4700	1·796	1·512	1·462
4600	1·876	1·616	1·57
4500	1·876	1·640	1·57
4400	2·068	1·624	1·48
4300	2·01	1·446	1·462
4200	2·046	1·233	1·462
4100	2·01	1·207	1·438
4000	1·828	1·192	1·264
3900	1·504	0·892	1·120
3800	1·296	0·650	0·674
3700	1·048	0·520	0·608
3600	0·695	0·384	0·372
3500	0·300	0·373	0·164

The screen referred to here is composed as follows :--

Gentian violet . . . . .	0'001 gram.
Acid green . . . . .	0'001 „
Diamond green . . . . .	0'0005 „
Water . . . . .	100 C.C.

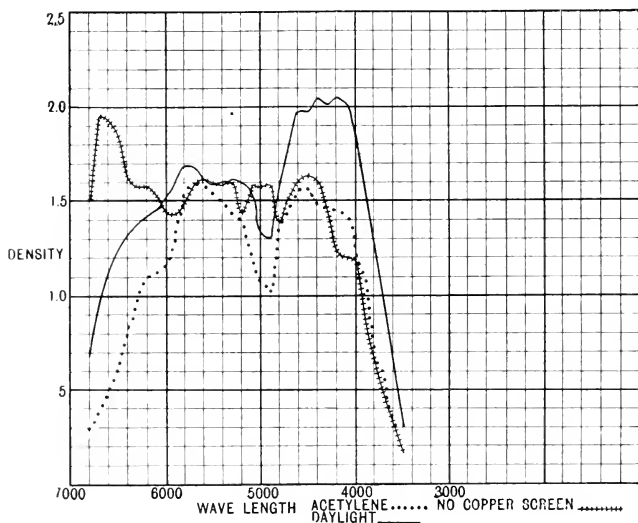


FIG. 56.

This screen was improved by increasing the gentian violet and also absorbing the green from 5000–5500 by means of rose bengal and mandarin orange. In order to avoid too much absorption at 6000, the diamond green was omitted.

The final form of this screen was—

A. <sup>1</sup> Gentian violet	$\frac{2}{100000}$	} 1 cm. thick.
Acid green	$\frac{1}{100000}$	
Mandarin orange	$\frac{1}{100000}$	
Rose bengal	$\frac{4}{1000000}$	

B. Copper acetate solution,  $1\frac{1}{2}$  per cent., 1 cm. thick.

<sup>1</sup> This A screen will not keep in gelatine, the gentian violet fading out.



And the absorption spectrum with the A screen as a gelatine-dyed screen was as follows :—

Wave-length.	E or D (Extinction coeffi- cient).	Wave-length.	E.
6800	1·724	5600	1·364
6700	1·710	5500	1·290
6600	1·640	5400	1·158
6500	1·630	5300	1·048
6400	1·580	5200	0·908
6300	1·520	5100	0·802
6200	1·432	5000	0·637
6100	1·490	4904	0·560
6000	1·570	4800	0·488
5900	1·580	4700	0·402
5800	1·512	4600	0·373
5700	1·408	4500	0·301

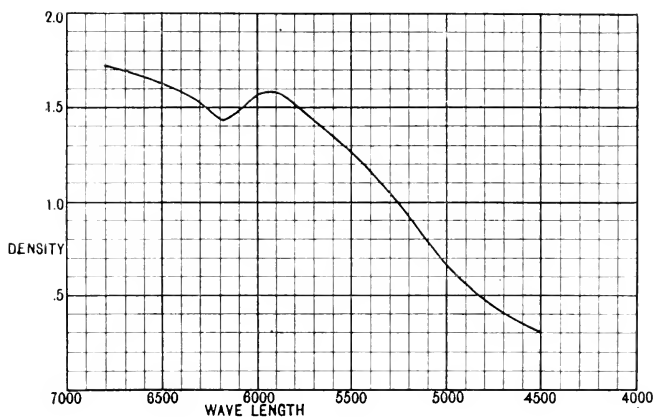


FIG. 57.

Using this screen, the following results were obtained for the spectrum curve of a pinacyanol bathed plate :—

Wave-length.	D.	D.	Wave-length.	D.	D.
	Daylight.	Screened acetylene.		Daylight.	Screened acetylene.
66	0·110	0·100	50	0·470	0·496
65	0·190	0·237	49	0·650	0·719
64	0·294	0·320	48	0·884	1·001
63	0·301	0·402	47	1·001	1·126
62	0·300	0·430	46	1·108	1·233
61	0·299	0·470	45	1·126	1·270
60	0·343	0·475	44	1·140	1·252
59	0·412	0·540	43	1·124	1·233
58	0·483	0·565	42	1·068	1·194
57	0·477	0·604	41	1·124	1·174
56	0·520	0·616	40	0·958	1·146
55	0·550	0·630	39	0·884	1·044
54	0·523	0·602	38	0·872	0·864
53	0·486	0·577	37	0·816	0·754
52	0·462	0·518	36	0·540	0·577
51	0·422	0·466	35	0·404	0·402

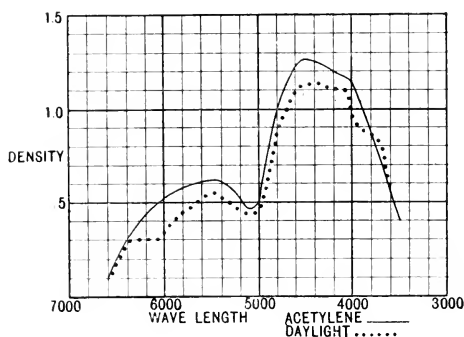


FIG. 58.

It will be seen from these results that the characteristics of daylight are reproduced by this screened acetylene light in a quite satisfactory manner; probably a closer agreement could be obtained if the daylight exposure were a trifle longer.

The experimental procedure for obtaining a spectrum curve is as follows:—In the dark slide of the Tallent spectroscope is a scale divided in wave-lengths and placed in such a position

that the indicated positions accurately correspond with the actual positions of spectral lines. This scale was kindly made by Mr. A. J. Bull.<sup>1</sup> The acetylene flame masked by the Methven screen<sup>2</sup> was then adjusted in front of a 4-inch condenser, which formed an image of the opening in the screen on the slit. A comparatively wide slit of about  $\frac{1}{10}$  mm. was used. The exposure was adjusted so that as full an exposure as possible was given without any trace of fogging from scattered light.

The negative is measured in the following way :—The two shutters of the plate carrier in the spectro-photometer (Fig. 11) having been shut down to a narrow slit about 2 mm. wide, a specially made carrier (Fig. 59) replaces the ordinary plate

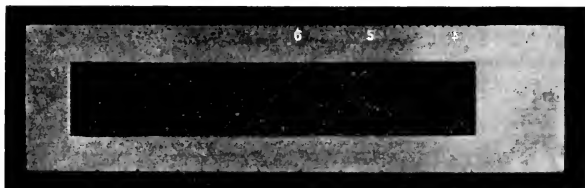


FIG. 59.

carrier A (Fig. 13). In this carrier there are a number of clicks for the spring catch which exactly correspond with the wavelength numbers impressed by the spectroscope and spaced to correspond throughout the whole spectrum, so that there is no difficulty in passing along the spectrum. With this fitting the plate can be measured easily and rapidly.

(b) The use of broad-banded filters for sensitometry. Assuming that what is required is something more than a density measurement under each filter, there are three possible

<sup>1</sup> For description of the making of the scale, see *Phot. Journ.*, October, 1903, p. 271, and *Phot. Journ.*, January, 1905, p. 17. The appearance of the finished spectra is exactly as shown in the illustrations to this latter paper.

<sup>2</sup> See *Phot. Journ.*, July, 1904, for description of the acetylene standard light ; also Part I. Chap. II.

methods of using broad-banded filters for the purposes of sensitometry.

These are, of course, the three systems of ordinary sensitometry, a graded set of densities, with an observation of the highest one which makes an impression, as in the Warnerke Sensitometer, a Scheiner wheel, and the measurement of the inertia as in Hurter and Driffeld's system.

There is no reason why the first system should not be extensively adopted; it is not an accurate one, but it is very rapid, and requires but little apparatus on training. It appears not to be used, however, the majority of workers resting content with spectrum tests. The second system is that worked out by Dr. Eder, and is most important.

Inasmuch as the sensitiveness of an undyed plate ends at about 5000–5100, we may use this point as the dividing point for the spectrum, and conclude that sensitiveness above this may be ascribed to the added dye in the case of a colour-sensitised plate.

The filters which Eder suggests are—

Yellow. 4 per cent. potassium chromate solution 1 cm. thick.

Blue. 2 per cent. copper sulphate solution saturated with ammonia 1 cm. thick.

The absorptions of these two filters have been measured with the following results:—

Wave-length.	D.	D.	Wave-length.	D.	D.
	Blue.	Yellow.		Blue.	Yellow.
5300	—	0	4800	0·798	—
5200	—	0·057	4700	0·602	—
5100	1·98	0·109	4600	0·448	—
5000	1·53	0·386	4500	0·310	—
4900	1·252	1·035	4400	0·212	—
4850	—	1·768	4300	0·070	—

(FIG. 60.)

On a Wratten Ordinary plate the ratio  $\frac{\text{blue sensitiveness}}{\text{yellow sensitiveness}}$  is  $\frac{112}{1}$ .

Dr. Eder uses these filters in the front of the Scheiner wheel, which is a sector-wheel having 23 openings, of which each pair bear to one another the ratio 1 : 1·27. After development the plate is laid on a sheet of white paper, and the last number visible is taken as the sensitiveness. Naturally the light-source used in this determination is of great importance, and the following table is taken from Eder<sup>1</sup> :—

Plate.	Lowest number visible.		Relative sensitiveness. Blue Yellow		
	Pentane lamp.	Daylight.	Pentane.	Reflected from white paper.	
				Diffused daylight.	Magnesium light.
Commercial orthochromatic plates (erythrosin).					
(a) Kolor . . . . .	19	10-11	$\frac{1}{4\cdot8}$	$\frac{1\cdot6-1\cdot9}{1}$	$\frac{1\cdot1-1\cdot3}{1}$
(b) Schatten . . . . .	19	11-12	$\frac{1}{4\cdot7-5\cdot5}$	$\frac{2\cdot7}{1}$	$\frac{1\cdot3-1\cdot6}{1}$
(c) Kodoid . . . . .	13	11-12	$\frac{1}{1\cdot3}$	$\frac{6-7}{1}$	$\frac{4\cdot3-5}{1}$
(d) Perorto . . . . .	15	9-10	$\frac{1}{3}$	$\frac{2\cdot8}{1}$	$\frac{1\cdot35}{1}$
(e) With dyed film acting as screen, Perxanto	14	7-8	$\frac{1}{8}$	$\frac{1\cdot2-1\cdot3}{1}$	—
(f) Lumière yellow green	12	9	$\frac{1}{1\cdot3} \quad \frac{1}{1\cdot1}$	$\frac{11\cdot3}{1}$	$\frac{4\cdot9}{1}$
Bad orange sensitive plates	10	7	$\frac{1}{2\cdot1-2\cdot4}$	$\frac{60}{1}$	$\frac{20}{1}$
Bad panchromatic plates	11	8	$\frac{1}{1\cdot8}$	$\frac{62}{1}$	—
Moderately good panchromatised emulsion plates	17	10-11	$\frac{1}{2\cdot1}$	$\frac{7\cdot1}{1}$	—
Orthochrom T or ethyl red bathed plates	18-19	11	$\frac{1}{4-5}$	$\frac{1}{1\cdot3}$	—

<sup>1</sup> J. M. Eder, *Beiträge zur Photo-Chemie*, Part II., p. 161.

Inasmuch as a system of sensitometry which depends on the observation of the last visible number must always be imperfect, it is preferable to determine the Hurter and Driffeld Inertia beneath each of the screens and to take the ratio of these inertias.

The ratio  $\frac{\text{yellow inertia}}{\text{blue inertia}} = \frac{\text{blue sensitiveness}}{\text{yellow sensitiveness}}$  may be termed  $\chi$  (*chrōma*, a colour).

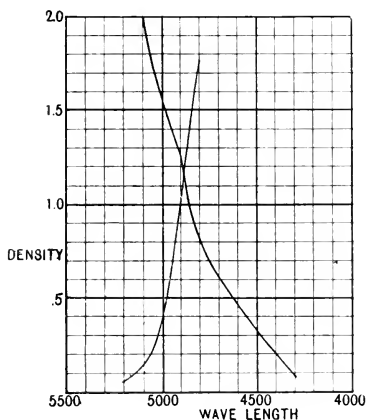


FIG. 60.

For most erythrosin plates the value of

$$\chi = 12 \text{ to } 20$$

For good panchromatic plates—

$$\chi = 5 \text{ to } 10$$

and for plates with subdued blue sensitiveness (generally slow)—

$$\chi = 2 \text{ to } 5$$

Bathing plates in various isocyanines, we obtained for  $\chi$ —

Pinachrome . . . . .	1.1
Pinaverdol . . . . .	2.1
Homocol . . . . .	1.1
Pinacyanol . . . . .	1.8

The value is not affected if the plates are dried with spirit after bathing.

A great cause of fog with these dyes appears to be found in the ammonia which is usually added. Though necessary with some plates, it may be omitted with advantage with most.

Other plates bathed in homocol gave—

Ilford Zenith,  $\chi = 1.52$ .

Wratten Speed,  $\chi = 2.32$ , and another lot  $\chi = 2.0$ .

The effect of isocyanines upon the general sensitiveness of plates to daylight appeared to be of interest, and the inertias of plates before and after bathing in homocol were therefore determined in the usual way.

### Results—

Plate.	Inertia.		Ratio. $\frac{\text{Unbathed inertia}}{\text{Bathed.}}$
	Bathed.	Unbathed.	
Ilford Half-tone . . .	2.40	2.35	0.98
Wratten Speed . . .	0.112	0.174	1.55
Eastman Extra Rapid .	0.192	0.099	0.518

The great differences in these results are probably due to the fact that the sensitiveness will depend upon the extent to which the dye is washed out.

In judging of the value of low numbers for  $\chi$  in the case of commercial plates, attention must always be paid to the total sensitiveness to blue light, since  $\chi$  can obviously be increased at the expense of total sensitiveness by dyeing the film yellow.

This method of measurement is useful in attempting to find the effect of colour sensitising with different dyes, and it enables one to quantitatively follow the effect of any alteration in procedure.

Thus the following attempt to bathe gelatine plates in

ethyl violet, the well-known sensitiser for collodion emulsion, is a good example of the use of  $\chi$ .

Wratten Ordinary plates were bathed in a  $\frac{1}{250000}$  solution of ethyl violet, rinsed and tested:— $\chi = 40$ .

Next a plate was bathed ten minutes in  $\frac{1}{50000}$  ethyl violet, rinsed and then washed five minutes in alcohol:— $\chi = 36$ . The effect of adding ammonia was tried:— $\chi = 40$ ; and fog was induced.

This was repeated with a rinse in alcohol:— $\chi = 10$ ; but the plates were foggy.

Generally, in fact, this measurement gives a quantitative expression of the extent of the sensitising which is greatly to be desired, and is notably absent from most spectrum tests.

The majority of commercial plates have practically no red sensitiveness, and the two-colour test gives almost all necessary information; but for plates bathed in the isocyanines the true red sensitiveness becomes of importance, and the two-colour test is insufficient. For three-colour photography it appears necessary to use overlapping filters, and in most sensitometric three-colour tests these filters have been used, but it is clearly wrong to allow any overlap in sensitometry. Take, for instance, a plate having a band of sensitiveness extending from 5700–5900. Then with the ordinary commercial three-colour filters this will be registered throughout through both the green and red screens, and will give a deceptive appearance of red sensitiveness to the plate. Consequently the ideal at which we must aim is abrupt absorption filters which do not give any appreciable overlap, and which should pass from red end to 5900, from 5900–5000, and from 5000 to blue end. The blue and green filters are easily obtained as solutions of inorganic salts, but attempts to obtain a red filter produced too gradual an absorption, and it was necessary to resort to dyes.

The blue screen is Eder's blue screen. The green screen consists of Eder's yellow screen to cut out the blue and a saturated solution of copper acetate to cut out the red. This screen is more transparent and has more abrupt absorption than any commercial dyed screen that has been examined.



The green screen has the following absorption curve :—

Wave-length.	E.	Wave-length.	E.
6150	2.50	5600	0.600
6100	2.25	5400	0.349
6050	1.930	5200	0.255
6000	1.734	5100	0.255
5950	1.650	5000	0.481
5900	1.401	4900	1.110
5800	1.099	4850	1.833
5700	0.852		

(FIG. 61.)

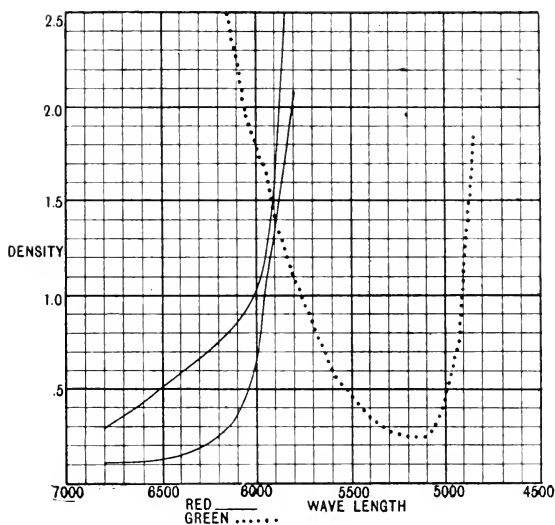


FIG. 61.

The first red screen was made of Eder's yellow screen and 1 cm. of an  $\frac{N}{50}$  solution of potassium permanganate. This gives absorptions as follows :—

Wave-length.	E.	Wave-length.	E.
7000	0'157	5950	1'233
6800	0'286	5925	1'408
6600	0'416	5900	1'624
6400	0'596	5875	2'022
6200	0'739	5850	2'51
6000	0'984		

(FIG. 61.)

There are two objections to this screen : in the first place, the absorption between 6600 and 6000 is much too great ; and in the second place, solutions of permanganate are unstable, and would necessitate continual checking.

It has been replaced by a dyed gelatine screen which was prepared by Mr. A. J. Newton, and is dyed with rose bengal and tartrazin. This is a very good screen, and gives the following absorptions :—

Wave-length.	E.	Wave-length.	E.
7000	0'112	6000	0'686
6800	0'116	5950	1'062
6600	0'121	5900	1'394
6400	0'140	5850	1'670
6200	0'243	5800	2'086

(FIG. 61.)

It will be observed that at 6200 this screen lets through three times as much light as the last.

The first measurements with these three-colour screens were made with the object of comparing daylight and screened acetylene. The plates to be measured were exposed for a sufficient period to obtain approximately equal exposures behind the three screens, and the inertias were measured.

The following results were obtained for the tri-colour ratios on a pinacyanol bathed plate :—

## DAYLIGHT AS LIGHT-SOURCE.

	Red.	Green.	Blue.
Log $i$ . . . .	1'74	1'97	0'50
$i$ . . . . .	55'0	93'9	3'16
Ratio . . . .	17'4	29'7	1'0

*Note.*—It must be remembered that this blue screen is very transparent, about five to ten times more transparent than Sanger Shepherd's blue screen, for instance, and much too transparent for practical use with moderately short exposures.

## (e) ACETYLENE UNSCREENED. (Not comparable with daylight.)

	Red.	Green.	Blue.
Log $i$ . . . .	0'50	1'13	0'40
$i$ . . . . .	3'16	13'5	2'52
Ratio . . . .	1'26	5'39	1'0

## ACETYLENE SCREENED TO DAYLIGHT BY SPECTROSCOPE.

	Red.	Green.	Blue.
Log $i$ . . . .	1'81	2'10	0'63
$i$ . . . . .	64'5	126'0	4'28
Ratio . . . .	15'1	29'5	1'0

The measurements for acetylene are not comparable with daylight as to absolute inertias; only the ratios are comparable.

Various measurements of the <sup>red inertia</sup>blue inertia were made under different conditions of daylight and for cloud-light in all cases; ratios varying from 12 to 17 were obtained.

The amount of ultra-violet light in daylight has also been measured by the following method:—

Plates (ordinary) were exposed behind the sector-wheel to daylight, with and without the following two screens:—

(1) 5 mm. of plate glass cutting at about 3300.

(2) 1 cm.  $\frac{1}{20000}$  potassium chromate solution cutting at 3950.

The tests were made to two forms of daylight as far apart as possible.

(a) Blue skylight.

(b) Direct sunlight. 3 o'clock, December 6th. Clear air.  
Six plates used.

1. Skylight	Unscreened.
2. „	Screen. (1)
3. „	Unscreened.
4. „	Screen. (2)
5. Sunlight	Unscreened.
6. „	Screen. (2)

Each pair of plates was exposed simultaneously, the screen being arranged to cover one plate only.

*Results—*

Plate.	1	2	3	4	5	6
Log <i>i</i> . . . .	0·74	0·87	0·46	0·85	0·08	0·40
Differences . .		0·13		0·39		0·32
Ratio of exposures		1·35		2·46		2·09

These results show clearly the large amount of ultra-violet in daylight, and also the small difference in the ultra-violet content of blue skylight and direct sunlight.

Any method of investigation of the colour-sensitiveness of plates tends to confirm the truth of Mallmann's early statement,<sup>1</sup> that the bath treatment for colour-sensitising is "the method of the future," and the introduction of the isocyanine sensitisers has made the treatment extremely simple and efficient.

The following experiments were made in order to find the best method of colour-sensitising a plate by bathing in an isocyanine :—

The measurement of the effect produced was made by finding the inertia of the plate under the red screen.

<sup>1</sup> "Orthochromatic Photography," *Phot. Journ.*, 1886, p. 123.

The plates were bathed by stirring in the dye in a thermostat for the given time and then washed by stirring in distilled water for their given time, wiped and exposed. Temperature of thermostat,  $20^{\circ}$  C. The dye used was pinacyanol.

(1) *The effect of the time of washing.*—Wratten Ordinary plates bathed in  $\frac{4}{100000}$  pinacyanol solution for three minutes.

Washed.	Inertia.
1. 0 minute . . . . .	20
2. 40 seconds . . . . .	5'14
3. 10 minutes . . . . .	1'26
4. 40 „ . . . . .	1'26

So that washing for ten minutes will produce the maximum effect.

(2) *The effect of the time of bathing.*—Plates bathed in  $\frac{4}{100000}$  pinacyanol for 1, 3, and 10 minutes, washed 10 minutes.

Bathed.	Inertia.
1 . . . . .	2'82
3 . . . . .	1'26
10 . . . . .	1'34

Therefore, provided the plate is bathed long enough, the time of bathing is of no importance; 3 minutes is long enough.

(3) *The effect of the concentration of the dye solution used.*—Plate bathed for 5 minutes in  $\frac{1}{100000}$ ,  $\frac{2}{100000}$ ,  $\frac{4}{100000}$ , and  $\frac{8}{100000}$  solutions of pinacyanol.

Washed 10 minutes.

Solution-strength per 100,000.	Inertia.
1 . . . . .	3'20
2 . . . . .	1'23
4 . . . . .	1'76
8 . . . . .	2'60

Whence we see that the  $\frac{2}{100000}$  solution gives the best results.

Thus the procedure to get maximum sensitiveness with pinacyanol is to bathe in  $\frac{2}{100000}$  solution for 3 minutes and wash at least 10 minutes.

Pinacyanol is a most valuable sensitiser, and is indeed almost the only dye which really confers a sensitiveness to the

red in any way comparable to that which is caused by erythrosin for the yellow-green.

This great sensitiveness extends to the extreme red, and in the solar spectrum the whole of the lines from the ultra-violet to B may be photographed with one exposure. Another of the newest isocyanines is dicyanin. This dye sensitises right up to 7600 from 5900, and the dye may be useful for spectrum photography in the infra-red.

The absorptions of the isocyanine dyes are of some interest inasmuch as these dyes obey Vogel's rule very well, and have sensitising bands displaced with regard to the absorption bands about 200 tenth-metres towards the red.

The absorptions of the dyes have been measured for 1 cm. thick solutions of the following strengths:—

Ethyl red . . . . .	$\frac{1}{4000}$	{ (a) Without ammonia. (b) With ammonia.
Orthochrome T. . . . .	$\frac{1}{10000}$	
Pinaverdol . . . . .	$\frac{1}{20000}$	
Pinachrome . . . . .	$\frac{1}{10000}$	
Homocol . . . . .	$\frac{1}{20000}$	
Pinacyanol . . . . .	$\frac{1}{100000}$	
Dicyanin . . . . .	$\frac{1}{100000}$	

They are plotted together in pairs for purposes of comparison.

Wave-length.	E.	E.	Wave-length.	E.	E.
	Ethyl red.	Orthochrome T.		Ethyl red.	Orthochrome
6300	0·081	—	5300	1·504	2·360
6200	0·110	—	5200	1·337	3·164
6100	0·270	0·053	5100	0·960	2·654
6000	0·464	0·170	5000	0·630	2·102
5900	0·725	0·236	4900	0·490	1·207
5800	1·462	0·625	4800	0·418	0·890
5700	2·18	1·408	4700	0·246	0·540
5600	2·38	3·36	4600	0·129	0·390
5500	1·804	2·83	4500	0·072	0·326
5400	1·520	2·336	—	—	—

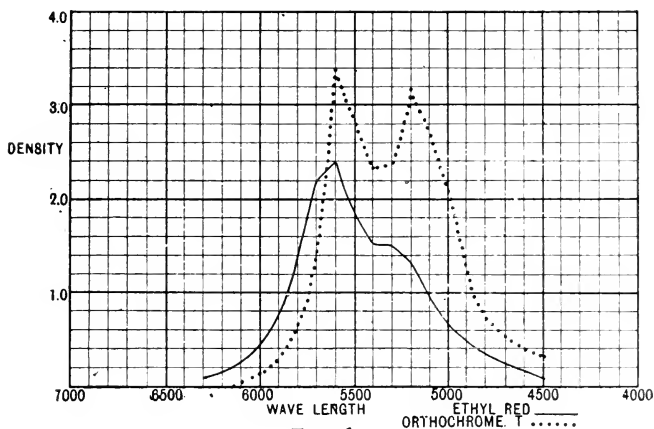


FIG. 62.

Wave-length.	E.	E.	Wave-length.	E.	E.
	Pinaverdol.	Dicyanin.		Pinaverdol.	Dicyanin.
6800	—	0'133	5600	2'40	1'034
6700	—	0'286	5500	2'120	0'880
6600	—	0'483	5400	2'046	0'590
6500	—	0'612	5300	2'40	0'442
6400	—	0'531	5200	2'506	0'252
6300	0'234	0'494	5100	2'00	0'143
6200	0'242	0'539	5000	1'504	—
6100	0'428	0'630	4900	1'252	—
6000	0'608	0'792	4800	0'900	—
5900	0'932	1'135	4700	0'802	—
5800	1'734	1'135	4600	0'650	—
5700	2'23	1'135	4500	0'542	—

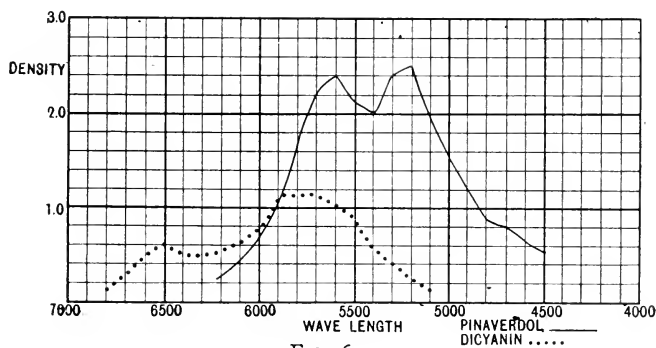


FIG. 63.

Wave-length (tenth-metres).	Homocol solution.		Wave-length (tenth-metres).	Homocol solution.	
	1 in 20,000. 1 cm. thickness.			1 in 20,000. 1 cm. thickness.	
	$E_a$ .	$E_b$ .		$E_a$ .	$E_b$ .
7000-6200	0'148	0'148	5200	1'330	3'340
6100	0'148	0'180	5100	1'200	3'460
6000	0'148	0'326	5000	1'120	3'360
5900	0'173	0'455	4900	0'996	2'760
5800	0'226	0'748	4800	0'872	2'192
5700	0'422	1'258	4700	0'639	1'350
5600	0'574	1'758	4600	0'574	0'984
5500	0'806	1'948	4500	0'312	0'710
5400	1'084	2'192	4400	0'202	0'432
5300	1'245	2'606	4300	0'085	0'238

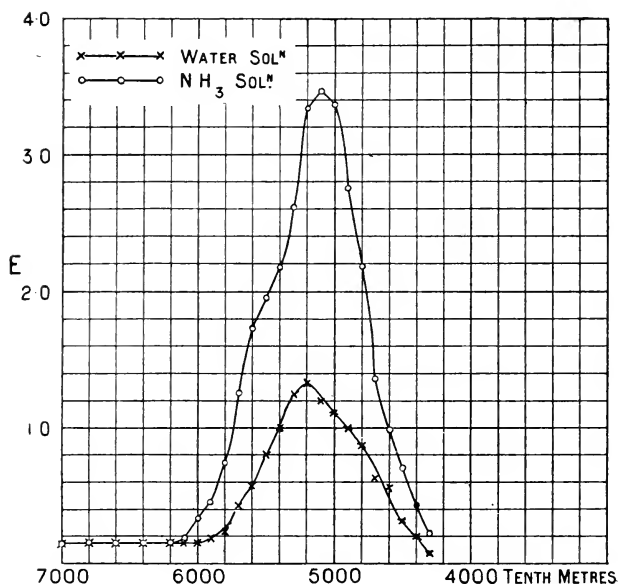


FIG. 64.



Wave-length.	E.	E.	Wave-length.	E.	E.
	Pinachrome.	Pinacyanol.		Pinachrome.	Pinacyanol.
6700	—	0'104	5500	1'722	2'312
6600	—	0'157	5400	1'541	1'962
6500	—	0'184	5300	1'945	1'624
6400	—	0'220	5200	2'595	1'470
6300	0'121	0'307	5100	1'904	1'135
6200	0'164	0'786	5000	1'239	0'796
6100	0'220	1'323	4900	1'032	0'508
6000	0'296	1'512	4800	0'817	0'432
5900	0'530	1'230	4700	0'738	0'258
5800	0'853	1'068	4600	0'504	0'163
5700	1'438	1'186	4500	0'429	0'119
5600	1'858	1'734			

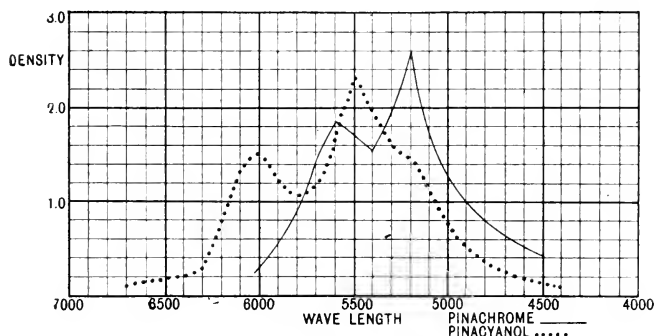


FIG. 65.

These absorption measurements, as well of those of the filters, etc., recorded in this chapter were rendered much easier by the adoption of a new principle which has been termed the method of compensating filters.

In the spectrophotometry of coloured substances, whether as solutions, screens, or pigments, there is great difficulty in making high readings, especially in the blue and violet, owing to the light scattered in the instruments from other portions of the spectrum.

*Example.*—Suppose a solution of chromic acid gives a density of 2.0 at 4800. Then the density will be obscured by scattered light reflected in the spectroscop from yellow, red,

and green portions of the spectrum having a visual luminosity of possibly 1000 times that which is to be measured. This makes measurements both difficult and inaccurate.

This difficulty may be overcome by using supplementary colour filters which absorb those portions of the spectrum which are not needed for measurements.

Suitable filters are given by the following solutions:—

From 4600—violet end .  $\frac{N}{100}$  potassium permanganate and saturated copper acetate.

4950—4600 . . .  $\frac{1}{15000}$  Gentian violet and saturated copper acetate.

5700—4950 . . . 4 per cent. potassium chromate and saturated copper acetate.

610—5700 . . . Dinormal chromic acid and half-saturated copper acetate.

Above 610 . . . . . Dark room red filters.

With the aid of these filters it is possible to make as high and as accurate measurements of the absorption of solutions as of photographic plates.

**The Theory of Colour Sensitisers.**—It has been clearly shown that the effect upon the spectrum sensitiveness of a plate which is produced by bathing the plate in a dyeing solution is closely related to the absorption of the dye employed. This is clearly borne out, for example, in the case of pinacyanol, where the absorption curve (Fig. 68) shows two maxima at 6000 and at 5500, and these are reproduced in a blurred condition in the sensitising curve by a maximum at 5500 and a hump at 6100. Eder has shown<sup>1</sup> that the difference between the absorption and sensitising maxima which occurs in most cases is due to the fact that the absorption of dyed silver bromide differs from that of the pure dye in accordance with Kundt's law. This being so, it would seem possible that all that is needed to change the sensitiveness of silver

<sup>1</sup> "Über das Verhalten der Haloïdverbindungen des Silbers gegen das Sonnenspectrum und die Steigerung ihrer Empfindlichkeit durch Farbstoffe," *Beiträge*, III. p. 1.

bromide with respect to the spectrum is that it shall have a different absorption, *i.e.* be dyed. In connection with this point it would be useful to know the distribution of sensitiveness with regard to the spectrum which might be shown by some strongly absorbing salt of silver. To this end the following experiment was performed :—

An emulsion was made as follows: To a 10 per cent. gelatine solution 13 per cent. potassium chromate was added, and then in the usual way 10 per cent. of silver nitrate. The emulsion was allowed to set, broken up and washed completely in a percolator and re-melted for coating. The plates were then dried, all the above operations having been performed in the dark room.

On exposure of the plates it was found that they were reduced all over at once by either an alkaline developer or by an acid ferrous sulphate developer, but that an exactly neutral solution of ferrous sulphate would reduce the light-exposed salt much more quickly than the unexposed chromate, *i.e.* silver chromate emulsion is light-sensitive and capable of forming a latent image. The speed of the plates was measured approximately and the inertia was found to be about 40,000 c.m.s.<sup>1</sup>

Of course a plate so slow as this could not be exposed to the spectrum, but it was exposed beneath green, yellow, and blue glasses, and gave almost equal densities beneath the three, so that this emulsion is strongly green-sensitive.

There is a probability that the sensitising power of a dye is connected with its instability to light, but quantitative confirmation appears to be lacking. Dicyanin, for instance, is extremely unstable, while Rose-Bengal is stable but a good sensitiser. So far as can be seen, the condition for a sensitiser is that it has an absorption band in the region for which it sensitises, and that it dyes the silver bromide itself and not merely the gelatine.<sup>2</sup>

<sup>1</sup> This has been repeated by S. H. Wratten and one of us for silver erythrosinate with the same results.

<sup>2</sup> For the bearing of the photo-electric effect on colour-sensitisers, *vide* p. 273.

**Spectro-Sensitometry.**—It was mentioned at the beginning of this chapter that it might be possible to combine the two methods of determining the distribution of sensitiveness of a plate into one complete system. Hitherto the experimental difficulties have prevented this, but as it now appears possible to overcome them, it will be convenient to suggest the method of procedure.

The unit of light which is used in sensitometry is a mixed unit composed of light of different wave-lengths and having no definite energy equivalent. Thus it may be composed of much energy in the form of long wave-length light or little energy of short wave-length.

But if light be resolved into a spectrum and the spectral sensitiveness of a plate measured, then for any wave-length the exposure given can be expressed in terms of work done, *i.e.* in absolute units of work. What amount of work is required there seems to be practically no evidence to show. Hurter's calculation gives on reduction about  $1 \times 10^9$  ergs of violet light per sq. cm. for a density of 1, but this number is probably too large.<sup>1</sup>

The work equivalent of a spectrum is capable of direct measurement by means of a bolometer or radiomicrometer, or it may be calculated from the total intensity by means of Wien and Planck's law for a large number of light-sources, but calculation is dangerous owing to the impossibility of allowing for selective absorption or reflection in the spectroscop.

The following experimental arrangement might be used: Arrange a plane grating spectroscop in front of a narrow slit so that any narrow band of the spectrum may be passed through the slit with certainty.

As light-source an acetylene flame turned edgewise will give a constant and intense light through the spectroscop slit.

Now, if this narrow band be allowed to fall upon the circuit of a Boys' radiomicrometer, the intensity of the incident light can be measured in heat units if the radiomicrometer be previously calibrated by means of a known heat-source. Then

<sup>1</sup> Energy values behind three colour filters have been given by J. Precht and E. Stenger, *Phys. Zeit.*, 1905, 6. 179.

if this energy curve for the spectrum be plotted, the integration of the curve over any area will give the total energy incident.

Now, let this spectroscope be erected in front of the sensitizer with suitable arrangements for obtaining even illumination. Then it can be used in two different ways—either we can measure the inertia of a plate throughout the whole spectrum, wave-length by wave-length, plotting our results in energy units; or, by using broad bands of light, we can obtain the integrating effect of broad-banded filters. The chief difficulty in this method is the great amount of time required to measure the plates so exposed. Thus one plate-test to the whole spectrum would require about 200 density measurements, and the plotting of from 15 to 30 separate curves, a serious task. It is hoped, however, that a new type of measuring photometer will remove this difficulty, and that the suggestions which have been briefly outlined above may be brought into practical use.

NOTE, March, 1907.—This chapter has been left in the same state as when published twelve months ago. It could not be brought up to date without entirely rewriting. On colour sensitising E. König has published his new edition of Vogel's "Photochemie." On colour sensitometry A. Callier has published a great deal of work on the lines of Eder's method. Belin has published a new method of colour sensitometry by the rotation of a small sector wheel in front of a spectroscope slit. And one of us has commercially introduced a series of bathed plates and filters.



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